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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP946

Part of Journal of Research of the National Bureau of Standards, Volume 17, December 1936

THE VALUE OF GRAVITY AT WASHINGTON

By Paul R. Heyl and Guy S. Cook

ABSTRACT

An absolute determination of the value of gravity in the constant-temperature room in the second subbasement of the East Building of the National Bureau of Standards has given the value 980.08 cm/sec². This determination was carried out with pendulums of fused silica, and special attention was directed to the flexure correction.

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I. INTRODUCTION

1. PURPOSE OF THE WORK

The work herein described was undertaken by the National Bureau of Standards at the request of the U. S. Coast and Geodetic Survey, in order to obtain by absolute measurement the value of gravity at the base station of the Survey in Washington. Prior to this work the value adopted by the Survey had rested upon relative comparisons with the absolute-gravity station at Potsdam, Germany. Several

such comparisons had given results for the Survey's old base station at 205 New Jersey Avenue SE., varying by as much as 9 parts in a million. In 1900 a direct connection of that station with Potsdam and other stations in Europe was made by G. R. Putnam. The value obtained for Washington was 980.112. More recently a connection was made with Ottawa, Canada, which had an independent connection with Potsdam, and the value obtained for Washington was 980.117. Again, when Dr. F. A. Vening Meinesz, of Holland, brought his gravity-at-sea apparatus to this country the value he found for Washington was 980.121. In view of these varying results it was felt that the Survey's adopted value of 980.112 was probably too small, and that an absolute determination at Washington should be undertaken.

During the progress of this work a new direct connection with Potsdam was made in 1933 by Lt. Brown of the Survey. His result, calculated in terms of the old station, which had then been abandoned by the Survey, was 980.118.

The National Bureau of Standards was interested in such a determination on its own account also, as the value of g enters into absolute electrical determinations such as that of the ampere by the current balance.

2. PREVIOUS ABSOLUTE DETERMINATIONS OF GRAVITY

Since the publication in 1906 of the result of the absolute determination of gravity at Potsdam that station by common consent has been the accepted international base. The Potsdam value superseded all previous results, such as those obtained in Austria and in Italy, and was regarded as the most precise and authoritative figure that had been obtained up to that time.

For this there was a special reason. All earlier determinations had involved an unrecognized error, arising from the flexure of the pendulum while swinging. Attention had been called to this point on purely theoretical grounds by C. S. Pierce [1] as early as 1884, but his calculated correction was so large as to seem incredible.

Ten years later the importance of this correction had been recognized by Helmert, whose calculations indicated that this error, while not as great as supposed by Pierce, was still to be regarded as one of the major corrections to be applied to the time of swing. In the case of a rather flexible pendulum which had been newly constructed but never used, Helmert found by his formula a correction of as much as 366 parts in a million in the value of g. For a pendulum that had been actually used for gravity determinations in France, Helmert calculated the flexure correction to be 18 parts per million.[2]

The recognition of the importance of this correction caused Helmert to give special attention to this point in the Potsdam determination of gravity. This work, begun in 1898, was carried out by Kühnen and Furtwängler under Helmert's supervision. The published report, dated 1906, fills a large volume.

3. PLAN OF THE PRESENT DETERMINATION

There appears as yet to be no better method available for the absolute determination of gravity than that of the reversible pendulum.

[1] U. S. Coast and Geodetic Survey, Report for 1884, Appendix 16.
[2] Helmert, Beiträge zur Theorie des Reversionspendels, p. 15 and 28, Potsdam, (1898).

Study was given to other possibilities, such as the ring pendulum of Mendenhall,[3] but none of these seemed sufficiently promising to be worthy of adoption.

Precision of length measurements would appear to call for as long a pendulum as possible, but this at present is about 1 meter. The use of a longer pendulum was felt to be inadvisable in view of the fact that the technique of measurement of lengths of 4 or more meters, especially in a vertical position, as is necessary in pendulum work, is not yet sufficiently perfected to give the precision that can be obtained with a length of 1 meter.

There is recorded [4] the use of a pendulum 21 meters long, but the precision attained in the length measurements was only 0.1 mm, about 1 part in 200,000, whereas with a length of 1 meter a precision of 1 part in a million can be reached. It is to be said, however, that the disturbances arising from the imperfections of the knife-edge, which (as will appear later) are serious, theoretically should diminish as the pendulum is made longer. Largely because of these errors the time of swing of a pendulum which superficially might appear capable of measurement to a precision much exceeding 1 part in a million, actually is limited to a precision less than that attainable in length measurements.

Because of the difficulty of measuring a length defined by two knife-edges, and because of the desirability of using several different knife-edges with the same pendulum, it was decided to use pendulums of the two-plane type. As was first shown by Bessel, this construction eliminates in theory the correction for radius of curvature of a knife edge.

One factor of uncertainty in pendulum work has always been the temperature correction. It was therefore decided to construct the three essential parts of the apparatus—the pendulum, the standard scale, and the backbone of the comparator—all of fused silica, thus rendering the temperature correction almost negligible.

II. THE OBSERVING ROOM

For the observing room there was available the constant-temperature vault of the National Bureau of Standards. This vault is that which was used in the recent redetermination of the constant of gravitation.[5] It contained a large and a small room. The clock was installed in the large room and the pendulum in the small room. An opening about 30 cm square in the partition wall allowed the observer at the pendulum to see the clock dial when necessary.

III. THE PENDULUM APPARATUS

1. THE PENDULUMS

The form of pendulum adopted was dictated by the nature of the material used (fused silica) and was of necessity simple. It was an approximation to a uniform straight rod supported at one end, for which there is a second point of support with the same time of swing, situated at a point two-thirds of the distance to the other end of the rod.

[3] Mendenhall, Memoirs of the National Academy of Sciences, **X**, 1st Memoir (1905).
[4] A. A. Ivanov, Annals of the Central Bureau of Weights and Measures, **11-12**, Leningrad. (1915-18.) (In Russian.)
[5] BS J. Research **5**, 1243 (1930) RP256.

Each pendulum was made of a tube of fused silica. Four such pendulums were constructed, with different diameters to give varying flexibilities. To determine the flexibility, the pendulum was supported at two points near its ends, and a weight applied at the center. The bending was too small to be measured directly, but was determined by observing with a telescope the image of a distant scale reflected in a mirror attached to the end of the pendulum. In order to compare the flexibilities of the different pendulums the quantity $Q\mu/EI$ was calculated, in which

Q=Cross sectional area of the tube.
μ=Density.
E=Young's modulus.
I=Moment of inertia of cross section.

The silica tubes of which the pendulums were made were not perfectly uniform in cross section, but the above described procedure will give average values of EI and of $Q\mu$ (the mass per unit length). Let D be the distance between the points of support and F the weight applied. Then, since the bending is very small, we have at a point distant x from the point of application of F:

$$\frac{d^2y}{dx^2}=\frac{\text{Bending moment}}{EI}=\frac{\frac{F}{2}\left(\frac{D}{2}-x\right)}{EI}$$

$$\frac{dy}{dx}=\frac{F}{2EI}\left(\frac{Dx}{2}-\frac{x^2}{2}\right)=\frac{F}{4EI}(Dx-x^2)$$

The constant of integration is zero since $dy/dx=0$ if $x=0$, i. e., at the point of application of F.

At the end of the pendulum where the mirror was mounted x is nearly $D/2$. At this point:

$$\frac{dy}{dx}=\frac{\text{observed angular displacement}}{2}=\alpha$$

We have then:

$$\frac{1}{EI}=\frac{16\alpha}{FD^2}$$

Table 1 gives the data necessary for the calculation of $Q\mu/EI$. The values of the relative flexibility in the last column are merely numbers proportional to $Q\mu/EI$. In measuring the value of α the distance from mirror to scale was from 1,000 to 1,300 cm.

TABLE 1.—*Properties of pendulums*

Pendulum number	Outside diameter	Inside diameter	D	Mass	$Q\mu$	F	α	$\frac{1}{EI}$	$\frac{Q\mu}{EI}\times10^{12}$	Relative flexibility
	cm	cm	cm	g	g/cm	*Dynes*	*Radians*			
1	4	3.4	153.6	1,130	7.4	6.86×10^6	0.000 24	2.4×10^{-13}	1.8	1.00
2	4.5	3.4	154	1,927	12.5	6.86×10^6	.000 13	1.3×10^{-13}	1.6	.89
3	5	3.6	161	3,620	22.5	2.24×10^6	.000 17	4.7×10^{-14}	1.1	.61
4	7	5.8	157.5	3,582	22.7	3.43×10^6	.000 11	2.1×10^{-14}	.5	.28

During the progress of the work pendulum no. 1 was broken, and the work was finished with the other three. The broken pendulum

was that one which, because of its greatest flexibility, would have had the least influence in determining the final result.

Each pendulum was provided with two planes, upon each of which it could be swung in turn. One of these planes was as near as possible to one end of the pendulum, and when swung on this plane the pendulum was said to be in the down position. The second plane was located approximately at the conjugate point giving the same time of swing, and when swung on this plane the pendulum was said to be in the up position. Planes of two materials were used, fused silica and stellite.

For the purpose of attaching the planes to the pendulum, openings of the size and shape shown in figure 1 were cut through both sides of the silica tube. Through the 10- by 20-mm opening was inserted a block (of silica or stellite) of that cross section and long enough to project slightly on each side of the tube. One face of this block was

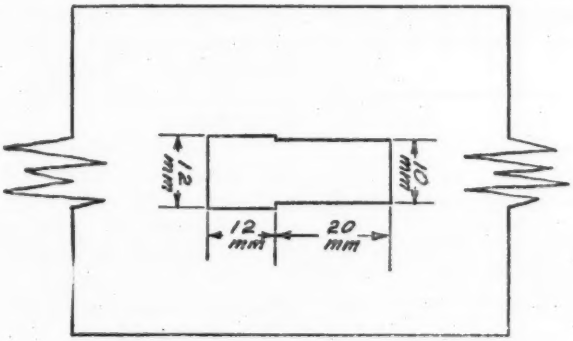

FIGURE 1.—*Opening in silica tube.*

worked optically flat and furnished the plane by which the pendulum rested upon the knife-edge. The knife-edge in its mounting was inserted through the 12- by 12-mm opening, which allowed sufficient room for the swinging of the pendulum.

The large 20-mm faces of the block were polished, but not to the same degree of flatness as the lower face. In the stellite blocks these faces served directly as mirrors for observing the flash signals in measuring the time of swing. With the silica blocks it was found advisable to attach small silvered glass mirrors to these faces.

In addition, the stellite blocks carried on both 20-mm faces a set of fine ruled lines as shown in figure 2, where the blocks are shown removed from the pendulum with their optically flat faces B, B in contact. While pressed closely together in this position the distance between the horizontal lines was determined for later use in measuring the length of the pendulum.

An attempt to rule such lines on the fused-silica blocks was not encouraging. This material does not take a ruled line well, the edges of the groove being ragged and irregular. Others have found this difficulty, and have attempted to overcome it by platinizing the silica surface and ruling lines through the platinum film only. Our experience with this has been that the lines are of nonuniform excellence, good in spots and ragged in others, due probably to a lack of uniformity in adhesion or thickness of the platinum film. For this reason we

adopted an indirect method of measuring the distance between silica blocks in the pendulum, which will be described later.

When the blocks were in place in the silica tube the mirror face and the set of measuring lines could be seen through openings cut in the tubes as shown in figure 3.

At the end faces of all the blocks vertical lines were ruled marking the median plane of the block. In setting up the pendulum these lines were so adjusted that their prolongations intersected that of the knife-edge, which could be done to 0.1 mm. The error in the value of g arising from a variation in this adjustment is not capable of calculation. It is irregular and seems to depend upon a variation in properties of the different places in the plane which may be in contact with the knife-edge. The experience of the U. S. Coast Survey has led them to attach special importance to this point in the construction of their instruments for relative gravity work. By the use of a mechanical device for raising and lowering the pendulum the Coast Survey found that the knife-edge could be set repeatedly on the same position on the plane, and relative values of g accurate to 1 part in a million could be obtained. Without this precaution the results varied widely and irregularly.

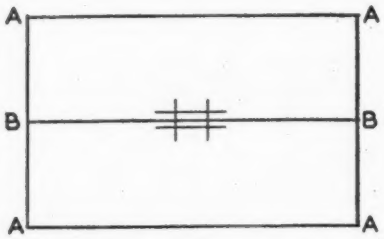

FIGURE 2.—*Stellite blocks with ruled lines.*

The blocks required mounting in the pendulum with the faces B,B parallel. This was attained by an optical method. The silica pendulum tube was mounted in a larger brass tube or jacket and held in place by setscrews with lead pads. This brass jacket was less than 100 cm long and enclosed that part of the silica tube between the places of support, allowing easy access to the holes and the blocks. The brass jacket was provided at each end with a circular ring or collar, on which the jacket and its contained silica tube could be rotated on a support consisting chiefly of two parallel rods. This arrangement made it possible to rotate the slightly irregular silica tube about a definite axis (fig. 3).

The silica tube was adjusted by means of the setscrews so as to be as nearly as possible concentric with the brass jacket. One of the blocks was then inserted in place and held by wooden wedges. A miniature 5-volt lamp was placed at the end of the silica tube and the image of the filament reflected from the face B of the block was observed with a telescope as the tube and brass jacket were rotated together. The image described a circle, showing that the plane B was not perpendicular to the axis of rotation.

Observation having indicated where the silica surfaces against which the face A,A rested needed grinding off, the block was removed and a little grinding done by means of a hand tool and a fine grade of carborundum powder. To facilitate this process the silica bearing surfaces were cut so as to offer a three-point bearing for the block, one silica surface being cut out slightly at its center and the other at its ends. The block was then replaced and another observation taken. It was found possible by repeated trials to adjust the block so that the reflected image remained nearly stationary on rotating the tube. The precision of this adjustment is indicated by the following figures.

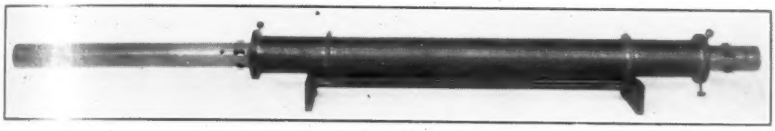

FIGURE 3.—*Brass jacket supporting silica tube.*

The lamp filament was about 2 mm long, and as the tube was rotated the radius of the circle described by the image of the filament was in no case greater than about one-fifth the length of the filament. The distance from telescope to mirror was, at one end of tube, about 120 cm, and at the other end about 170 cm. The maximum departure from parallelism indicated by these figures is about 0.01°.

A departure from parallelism in the direction of the swing of the pendulum, perpendicular to the knife-edge, is of no importance. A departure in the direction of the knife-edge reduces the problem to that of the horizontal pendulum. As shown by Webster (Dynamics, p. 252) the length of the equivalent simple pendulum is increased in the ratio $1/\cos\theta$, where θ is the angle made by the knife-edge with the horizontal. When $\theta=0.01°$, $\cos\theta=0.999\ 999\ 99$, and the correction is negligible.

Without disturbing the pendulum in its jacket the same process was carried out with the second block in its proper place. Each face B was thus set perpendicular to the same straight line, the joint axis of rotation of the tube and jacket, and hence the two faces B were parallel.

The blocks, held in position by wooden wedges, were then fastened in place by a suitable cement, none of which was allowed to reach the surfaces A,A. The best cement found for joining stellite to fused silica was red sealing wax. For joining silica to silica the best cement is fused chloride of silver, which melts at a moderate temperature.

It was possible to check the parallelism of the faces B,B after cementing by observing the reflection of the 5-volt lamp from one block with the other in place, there being sufficient space above and below the blocks to allow of this.

The next adjustment of the pendulum was that for equal times of swing on the two planes of support. To attain this, the silica tube, originally longer than necessary, was shortened by cutting off successive slices from its lower end, and finished by grinding slightly. A very accurate adjustment is thus easily possible. The necessity for this adjustment arises from the fact that the location of the center of gravity of the pendulum is not capable of determination with great accuracy. This defect may be counterbalanced by a sufficiently close adjustment of the two times of swing. The necessary approximation to equality of times is easily calculated.

The time of swing τ of the simple pendulum equivalent to a reversible pendulum of times of swing T_1 and T_2 is given by the formula:

$$\tau^2=\frac{T_1^2h_1-T_2^2h_2}{h_1-h_2} \quad . \quad . \quad . \quad . \quad . \tag{1}$$

where h_1 and h_2 are the distances of the center of gravity from the two planes of support. If l is the distance between these two planes, $h_2=l-h_1$ and eq 1 becomes

$$\tau^2=\frac{T_1^2h_1-T_2^2l+T_2^2h_1}{2h_1-l} \quad . \quad . \quad . \quad . \quad . \tag{2}$$

Differentiating and reducing:

$$\frac{d(\tau^2)}{dh_1}=\frac{(T_2^2-T_1^2)l}{(h_1-h_2)^2}$$

If τ is equal to $(T_1+T_2)/2$, as will essentially be the case if τ, T_1 and T_2 are each nearly unity,

$$\frac{d\tau}{dh_1}=\frac{(T_2-T_1)l}{(h_1-h_2)^2} \quad \ldots \ldots \quad (3)$$

As a numerical example, let $l=1{,}000$ mm, $h_1=700$ mm, $h_2=300$ mm, and $T_2-T_1=0.0001$ second. Then

$$\frac{d\tau}{dh_1}=0.000\,000\,6$$

Thus an error dh_1 of as much as 1 mm in locating the center of gravity would make a difference in the time of swing of but 6 parts in 10 million. As the center of gravity of the pendulum could be readily located to one- or two-tenths of a millimeter an adjustment of the times to 0.0001 second is sufficient for our purpose.

The theory of the reversible pendulum requires that the center of gravity shall lie in the plane of the two lines of support. When this is fulfilled, other asymmetries in a pendulum of the form used by us, in which there are no interchangeable weights, are (in a vacuum) self-eliminating. This adjustment was tested as was done in the Potsdam determination, after the pendulums were adjusted to equality of times of swing, by hanging each pendulum on a knife-edge with fine plumb lines passing close to the ends of the blocks. When the lines on the upper block coincided with the plumb lines, those on the lower block were in no case more than 0.2 mm out of line. A departure of 0.2 mm in 1,000 mm is geometrically of no importance as the cosine of the angle is 0.999 999 98.

The temperature coefficient of expansion of fused silica was taken to be 0.000 000 6, and this will of course be the coefficient for a pendulum with silica blocks. With stellite blocks in a silica pendulum it is a more complicated question. The coefficient of expansion of stellite varies with different samples from 0.000 011 to 0.000 015. The value 0.000 013 was assumed in this case.

Assuming the blocks to be always in contact with the silica bearing surfaces, and any differential expansion along the 2 cm width of the block to be taken up by the cement, we may calculate the net change of length between the planes of support B. Taking the distance between these planes to be approximately 100 cm we have:

$$104\times 0.000\,000\,6-4\times 0.000\,013=0.000\,062-0.000\,052=0.000\,010$$

Dividing by the length, 100 cm, we obtain for the coefficient of expansion 0.000 000 1, about one-sixth that of an all-silica pendulum. Assuming the value 0.000 011 for the coefficient of stellite, the coefficient of the pendulum becomes 0.000 000 18.

The temperature coefficient of time of swing will not be the same as that of linear expansion. For an all-silica pendulum, since the time of swing is proportional to the square root of the length, the time coefficient will be one-half the length coefficient, or 0.000 000 3. For a silica pendulum with stellite blocks the matter is not quite so simple.

Since the mass of a stellite block is small compared to that of the pendulum (from 4 to 8 percent) we may (as far as mass is concerned)

assume the pendulum, swung in either position, to be a uniform rod, pivoted at a distance h from its center of gravity. The radius of gyration of the pendulum about an axis through its center of gravity will be denoted by k. For a uniform rod, $k^2=L^2/12$, where L is the total length of the rod. The time of swing in either position will be given by

$$T^2=\frac{\pi^2}{g}\left(\frac{k^2+h^2}{h}\right)=\frac{\pi^2}{g}\left(\frac{L^2}{12h}+h\right)$$

Differentiating with respect to the temperature t:

$$\frac{d(T^2)}{dt}=\frac{\pi^2}{g}\left[\frac{12h\times 2L\frac{dL}{dt}-L^2\times 12\frac{dh}{dt}}{12^2h^2}+\frac{dh}{dt}\right]$$

Since T is nearly 1 second:

$$\frac{dT}{dt}=\frac{\pi^2}{2g}\left[\frac{L}{6h}\frac{dL}{dt}+\frac{dh}{dt}\left(1-\frac{L^2}{12h^2}\right)\right] \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

In all the pendulums we have approximately

$$L=155 \text{ cm}$$
$$h=70 \text{ cm (down)}$$
$$h=30 \text{ cm (up)}$$

In the down position we have, therefore,

$$\frac{L}{6h}=0.37$$

$$\frac{L^2}{12h^2}=0.41$$

$$\frac{dL}{dt}=155\times 0.000\ 000\ 6=0.000\ 093$$

$$\frac{dh}{dt}=72\times 0.000\ 000\ 6-2\times 0.000\ 013=0.000\ 017$$

Substituting in eq 4

$$\frac{dT}{dt}=0.000\ 000\ 22 \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

For the up position

$$h=30 \text{ cm}$$

$$\frac{L}{6h}=0.86$$

$$\frac{L^2}{12h^2}=2.22$$

$$\frac{dh}{dt}=32\times 0.000\ 000\ 6-2\times 0.000\ 013=-0.000\ 007$$

Substituting in eq 4

$$\frac{dT}{dt}=0.000\ 000\ 45\ .\ .\ .\ .\ .\qquad(6)$$

As a check on eq 4 we may calculate the time coefficients for an all-silica pendulum in the two positions. In the down position $dh/dt=70\times 0.000\ 000\ 6=0.000\ 042$ and in the up position $dh/dt=30\times 0.000\ 000\ 6=0.000\ 018$. The other quantities remain the same. Substituting in eq 4 the coefficient in each position comes out 0.000 000 29, a satisfactory agreement with 0.000 000 3, obtained by taking half of the coefficient of linear expansion.

The temperature corrections to the time of swing given by eq 5 and 6 were applied to each time of swing, down and up, as these were obtained, and the corrected values of T_1 and T_2 thus obtained were used in eq 1 to calculate τ^2 and finally g. No correction of h_1 or h_2 for temperature is necessary in eq 1, as the h values need be known only to four figures to insure a value of g accurate to 1 point in a million.

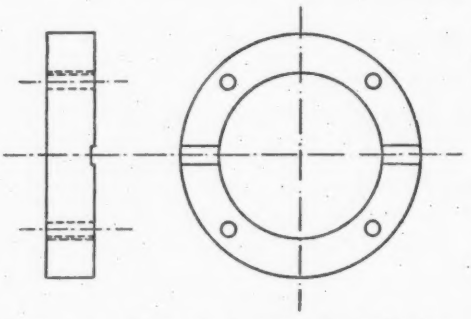

FIGURE 4.—*Brass ring support for knife-edge.*

2. THE SUPPORTING APPARATUS AND VACUUM CASE

The knife-edge upon which the pendulum swung was mounted in a steel support (later to be described) of such a size that it could pass through the 12-mm-square hole in the pendulum with room enough to spare for a reasonably large amplitude of swing. This steel support rested at its ends in notches cut in a heavy brass ring (fig. 4), which in turn was screwed down over a hole in a heavy steel shelf which rested on large cast-iron wall brackets (fig. 5).

The shelf and bracket supporting the pendulum were made especially massive and rigid in order that any motion of the support arising from the swinging of the pendulum should be as little as possible. The cast-iron brackets, weighing about 50 kg each, were bolted into a large mass of concrete imbedded in the brick wall of the room. The wall was hollowed out to a depth of about 75 cm, the cavity being made wider as it became deeper, dental fashion. Boards were placed across the cavity, which was about 1 meter square, and bolts set in proper position in one of the boards with their heads in the cavity. The cavity was then filled with concrete. When the boards were removed the brackets were fitted over the projecting bolts and fastened in place by nuts.

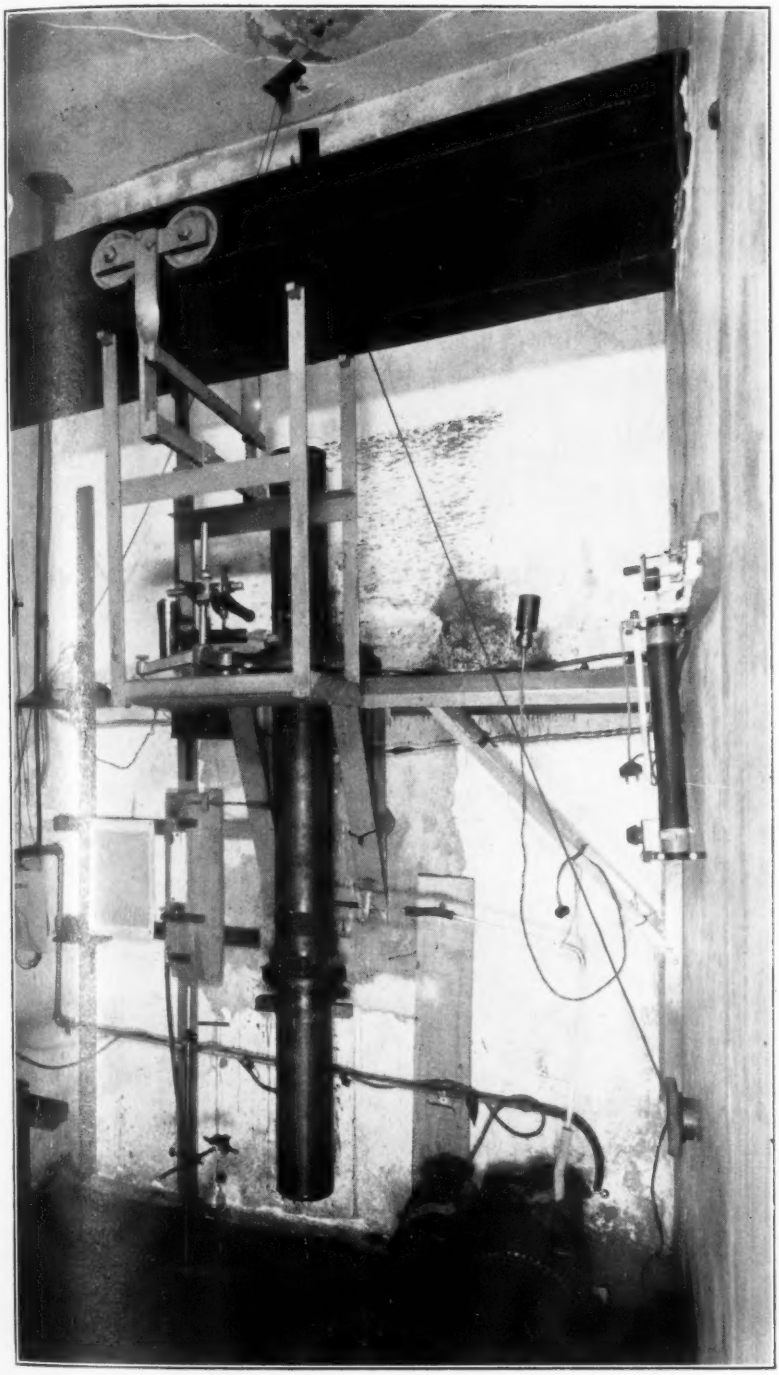

FIGURE 6.—*Vacuum case for pendulum.*

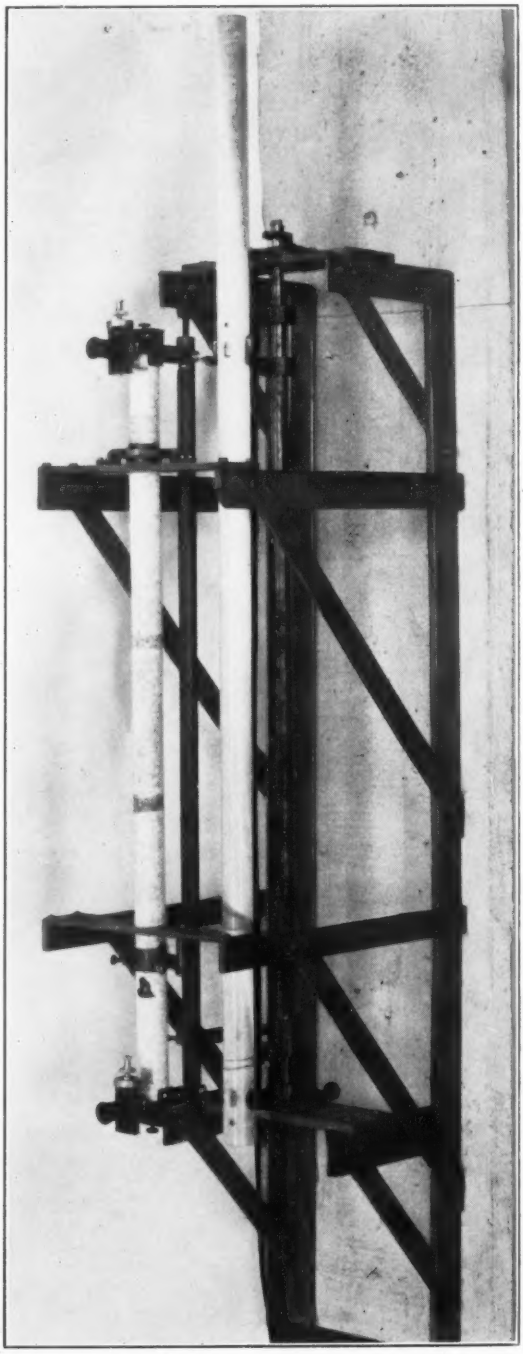

FIGURE 9.—*Comparator.*

The steel shelf resting on these brackets was 40 cm square and 4 cm thick, with a circular hole 9 cm in diameter over which the brass ring was fitted. This ring carried two bolts 180° apart which passed loosely through the ring and screwed into the steel shelf. There were also two other bolts at 90° from the first pair which screwed through the ring and pushed against the shelf. By means of these pulling and pushing bolts the ring and knife-edge could be levelled.

A departure from level would theoretically alter the time of swing. If θ is the angle made by the knife-edge with the horizontal the length of the equivalent simple pendulum will be increased in the ratio $1/\cos\theta$. The level used would indicate a difference of 0.001 radian, of which the cosine differs from unity by 5 parts in 10 million.

Apart from this geometrical effect there is the possibility of disturbing the time of swing by increasing the pressure on one-half of the knife-edge and decreasing it on the other. A number of experiments were made to test this point. Thin slips of sheet metal were

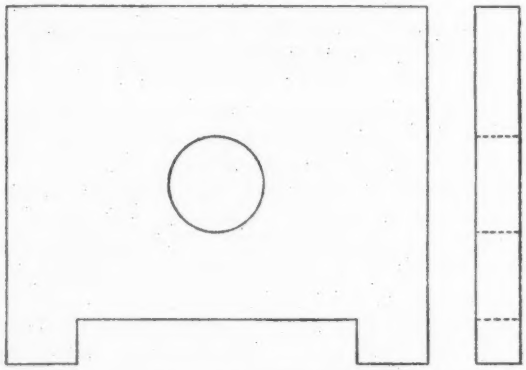

FIGURE 5.—*Steel shelf.*

inserted under one end or the other of the knife-edge, by which the level could be altered by steps of 0.001 radian. With differences of as much as 0.004 radian or more on either side there was always a consistent diminution of the time of swing, but for angles differing only 0.001 or 0.002 from the bubble level the effects were entirely irregular and of the same order of magnitude as were encountered in different settings at the bubble level.

The vacuum case was of brass tubing 16 cm inside diameter, and was made in three sections (fig. 6). The central section was bolted at its upper end to the underside of the steel shelf, and to its lower end was bolted the bottom section. The upper section rested by its own weight on the upper side of the steel shelf. Joints were made air-tight by a rosin-beeswax mixture.

The central and lower sections of the vacuum case were never removed from position, but the upper section had to be lifted and swung away every time the pendulum was to be reversed. For this purpose a pulley arrangement was provided.

Glass windows were provided in the pendulum case wherever necessary, such as where flash observations for coincidences were to be made, or where the amplitude of swing was to be measured. In the early stages of the work the amplitude was measured by observing the lower part of the pendulum by means of a traveling microscope.

Later this measurement was made by a beam of light reflected from the upper stellite or silica block to a scale about a meter away.

Outlets were provided in the central section for the pump connection and for the pressure gage. A gage of the McLeod type was used. Another outlet in the bottom section was provided with a glass stopcock which served as a pneumatic starter for the pendulum. In the early stages of the exhaustion puffs of air were admitted through this outlet in time with the swings of the pendulum until a suitable amplitude was obtained. The stopcock was then closed and the exhaustion finished to less than 0.1 mm.

Early in the work a quantity of radioactive sand was placed in the bottom of the vacuum case to provide against electrification of the pendulum. On comparing results obtained before and after introducing the sand there was no evidence that it was needed. However, it was allowed to remain in the case for the whole duration of the work.

3. THE KNIFE-EDGES

Several materials were tried for knife-edges—fused silica, agate, stellite, and steel. The behavior of these different materials will be later described.

The silica and agate edges were mounted in a groove in a bar of steel, and held in place either by cement or clamping pieces of metal. The stellite and steel edges were made in one piece, long enough to rest in the grooves in the brass ring and heavy enough to bear the weight of the pendulum, about 1 cm wide and high. The working edge was ground to an angle of about 135°, and was cut away for a space of from 1 to 2 cm in the middle to prevent walking of the pendulums.

No knife-edge can be ground to a geometrically perfect edge, nor is it advisable that it should be. On such an edge any finite load, however small, would produce an infinite pressure and a consequent breakdown of the edge. In Zeitschrift für Instrumentenkunde, January 1932, Schmerwitz describes a method for measuring the radius of curvature of a knife-edge. We have constructed an apparatus such as was used by Schmerwitz and find that his method can be used in practice with an accuracy of about 15 percent. Values for the radius of knife-edges, to be mentioned later, were obtained in this way.

IV. MEASUREMENT OF LENGTH

1. THE STANDARD SCALE

The standard scale was constructed of a piece of fused-silica tubing about 18 mm in diameter and a little over 1 m long. Near each end the tube was cut half way through and a flat silica plate fastened by fusion in the diametral plane of the tube (fig. 7). These plates were about 12 mm wide and were so placed that their centers were about 995 mm apart.

Silica scales have been constructed and observed over a considerable period of time at the National Physical Laboratory, in England, where it was found, as we have also observed (section III: 1), that silica does not receive or preserve graduations well, the material tending to flake off at the scratches. For this reason the National Physical Laboratory platinized portions of the silica surface and ruled lines through the thin coat of platinum without scratching the silica beneath.

This plan was tried by us, but difficulty was found in obtaining a coat of platinum that would give good lines at all places. Usually spots could be found upon which excellent lines could be ruled, but at other places it was not possible to do so well. For this reason a different plan was finally adopted.

The Hanovia Chemical and Manufacturing Co. constructed for us a scale with short pieces of tungsten rod fused into the flat silica plates. To these tungsten rods pieces of sheet platinum about 1 mm thick were silver-soldered. After polishing the faces of the platinum pieces it was found possible to rule excellent lines upon them. Lines were ruled approximately 0.25 mm apart, giving lengths varying from

FIGURE 7.—*Cross section of silica scale.*

about 994 to 999 mm. This scale was calibrated by comparison with a standard meter bar in the Length Section of the National Bureau of Standards. A copy of the report of these measurements follows.

INTERVALS ON PLATINUM-FACED SILICA SCALE

IDENTIFICATION NO. 2

(Graduated by National Bureau of Standards, Division II–1)

This bar, when supported at the two neutral points, has been compared with the standards of the United States, and the intervals indicated were found to have the following lengths at 20° C.

Intervals	Length (mm)
0 to 0	993. 9869
5 to 5	996. 4866
10 to 10	998. 9812

Left-end intervals	Length	Right-end intervals	Length
	mm		mm
0 to 1	0. 2502	0 to 1	0. 2498
1 to 2	. 2490	1 to 2	. 2504
2 to 3	. 2502	2 to 3	. 2503
3 to 4	. 2494	3 to 4	. 2495
4 to 5	. 2504	4 to 5	. 2494
5 to 6	. 2490	5 to 6	. 2500
6 to 7	. 2495	6 to 7	. 2477
7 to 8	. 2493	7 to 8	. 2540
8 to 9	. 2503	8 to 9	. 2497
9 to 10	. 2475	9 to 10	. 2491

The above values are not in error by more than 0.0010 mm.

The observations were taken at a mean temperature of 28.30° C and in reducing to 20° C the coefficient of expansion of the silica bar was assumed to be 0.000 000 6 per degree centigrade.

The scale was mounted for protection in a brass tube with openings to permit the graduated portions to be seen. Since the scale was to be used in a vertical position the brass tube was so arranged that the scale could be supported at either the bottom or the top. A series of observations failed to show any observable difference in the length in the two cases. Calculations indicated that such a change would be a small fraction of 1 micron, and our length measurements were good only to 1 micron. As a matter of convenience, therefore, the scale was always supported at the bottom.

2. THE MICROSCOPES

Two micrometer microscopes, of the Geneva Society's make, were employed in this work. Rather a long focus (about 2.5 cm) was necessary in order to reach the blocks inside the pendulum tubes. These microscopes were tested by the Length Section of the National Bureau of Standards for periodic and progressive errors and for the average value of one revolution of the drum, which carried 100 divisions. In each case the error was found to be less than one division on the drum. Each microscope was adjusted so that one revolution equalled 100 μ to better than 1 part in 1,000. The microscopes were provided with vertical illumination.

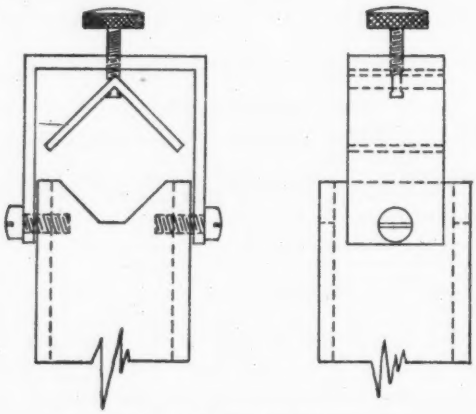

FIGURE 8.—*Clamp for microscopes.*

3. THE COMPARATOR

The comparator was built to handle the scale and pendulum in a vertical position. The most important part was the backbone which carried the two microscopes. This was made of a piece of silica tubing 3.5 cm in outside diameter, with walls about 4 mm thick. At the ends of the tube V-shaped notches were cut in which the microscopes were held by a clamp of the form shown in figure 8. This backbone was mounted in the metal framework of the comparator in a vertical position, held near its upper end by a brass collar in a gimbal bearing, and fastened near its lower end by three setscrews pressing against a second brass collar. Both collars were fastened to the tube by DeKhotinsky cement.

In the measurement of an all-silica pendulum against a silica scale there is no differential temperature coefficient of importance. The coefficient of different samples of fused silica at 20° C may vary by 2 parts in 10^7, while the precision of our measurements does not exceed 1 part in 10^6. Nor is the question of temperature gradients serious. As may be seen in fig. 9, the pendulum, the silica scale, and the backbone of the comparator were all within about 15 cm of each other.

With the pendulums carrying stellite blocks the case will be different. The coefficient of expansion of fused silica being 0.000 000 6 and that of the pendulum (see section III, 1) 0.000 000 1, it follows that there will be a differential expansion coefficient of the scale over that of the pendulum of 0.000 000 5. A knowledge of the temperature to the nearest degree would therefore ensure a precision in the comparison of scale and pendulum to 1 part in 2 million. As a matter of fact the temperature was always read to tenths of a degree. The temperature in the observing room changed by so small a fraction of a degree during such a comparison that the expansion of the comparator backbone was of no consequence.

For the general structure of the comparator a comparatively brief description will suffice. Its general appearance is shown in figure 9. The pendulum and scale were supported side by side by means of short arms projecting radially from a vertical rod. By turning this rod either pendulum or scale could be brought into view in the microscopes. Focusing was done by moving this vertical axis forward or backward at each end by a screw motion, the microscopes remaining fixed in position. The vertical axis could also be raised or lowered as desired.

The length of the silica backbone was adjusted so that the measuring lines on the pendulum appeared near the center of the field of each microscope. To allow for slight differences in the length of the different pendulums thin sheets of copper or aluminum were introduced between the microscope barrel and the notch in which it rested in the silica tube.

The pendulum was supported in the comparator at its upper plane upon a brass strip with a small vertical projection at its center, thus allowing the pendulum freedom of motion in two directions for purposes of alignment. At its lower end the pendulum was held by a rubber band against two setscrews in a Y-shaped support. By means of these screws and the upper pivot support the pendulum could be adjusted to the vertical. In addition, coarse adjustment was possible by rotating separately the projecting radial arms carrying the pendulum about the central axis of the comparator.

4. METHODS EMPLOYED

The measurement of the distance between the planes was most easily carried out with the stellite blocks. Before inserting the blocks in the pendulum they were pressed together at their optically flat surfaces and the distance between the ruled lines determined (fig. 2). After the blocks were set in place measurements were made on both

the front and back sides to eliminate any lack of parallelism. A typical example of such a length measurement follows:

Back position. Temperature 24.3°

Scale distance used, 997.9854 mm at 20.0°

Micrometer microscope readings, mm:

Pendulum			Scale		
	Lower	Upper		Lower	Upper
	0.6467	0.3550		0.7101	0.3804
	.6465	.3544		.7102	.3804
	.6467	.3540		.7102	.3804
	.6467	.3542		.7100	.3806
	.6464	.3548		.7101	.3802
Mean	0.6466	0.3545	Mean	0.7101	0.3804
	0.3545			0.3804	
$\Delta P =$	0.2921		$\Delta S =$	0.3297	
			$\Delta P =$	0.2921	

Scale-pendulum = 0.0376 mm at 24.3°
= 0.0354 at 20.0°
Scale = 997.9854 at 20.0°

Pendulum = 997.9500 at 20.0° between lines
Correction for lines 0.799

Length between planes = 997.151 mm at 20.0°

In the foregoing example the quantity ΔP is the amount to be added to the distance between the zero points of the microscopes to give the distance between the measuring lines on the pendulum, and ΔS is a similar quantity for the scale. By subtraction we obtain the difference between the scale and the pendulum.

In the case of the pendulums provided with silica blocks the measurement of length offers more difficulties. It is not practicable to rule lines on fused silica (section III, 1) and the first method tried for measuring the distance between the planes was Fizeau's "point and image" method used in end-standard measurements. In this method the point of a needle is placed against the plane and the cross wire of the microscope set on the junction of the point and its reflected image.

This method offers considerable experimental difficulty. Much depends on the precision of focusing, and as but half the lens is used, an objective of high perfection is required. Berndt-Schulz (Grundlagen und Geräte technischer Längenmessungen, page 23) says: "In spite of this, the precision of optical measurements on end-standards is about 5 times less than on line standards * * *. By the use of other objectives the error may be as large as 3.5 μ."

The end-standards spoken of here are the polished faces of metal bars. Rather unexpectedly, we have found that the difficulty is still further multiplied when dealing with transparent materials such as fused silica. The same microscopes that will give acceptable results on metal faces give abnormally variable results on faces of fused silica. In one case it was observed (through the microscope)

that as the needle steadily approached the surface its image halted for an instant and then resumed its motion.

It being thus out of the question to apply the "point and image" method to fused silica, recourse was had to contact blocks. Two small blocks of stainless steel were ruled with lines close to their edges, as with the stellite blocks, and the distance between the lines was determined when the blocks were pressed together. By a suitable clamping device one stainless steel block was pressed tightly against each silica block. In this way the problem was converted from one of an end-standard to one of a line standard.

V. MEASUREMENT OF TIME

1. THE CLOCK

A Shortt clock was employed to furnish second signals for the measurement of the time of swing. This form of clock and its performance are so well known from the work of Loomis [6] that no additional description is called for. In setting up the master clock in the large room of the constant temperature vault it was found necessary to enclose it in a thermostatically regulated case as a precaution against the presence of the observer with a light burning. The small room in which the pendulum was swung was kept dark and was entered only to observe coincidences.

2. THE TIME-SIGNAL SYSTEM

The use of mechanical relays in transmitting time signals is to be avoided in precision work. The variable friction involved in the moving parts and the fluctuations in the strength of the current that operates the relay usually combine to produce errors of several thousandths of a second. For the rating of a clock such errors may be of little importance, but for coincidence observations they are more serious. For this reason the time-signal system was arranged to give second signals without involving moving parts.

The case of the master clock was provided with a plate-glass bottom through which a beam of light was reflected from a small concave mirror attached to the lower end of the pendulum. The source of light was a straight-filament lamp, and the reflected image of the filament passed back and forth across a photoelectric cell contained in a brass tube provided with an adjustable slit. The electrical impulses from this cell were amplified until the energy was sufficient to operate either the flash system or the chronograph used for rating the clock.

The flash system employed was a neon-glow lamp mounted near the case in which the pendulum was swinging. By a simple optical system the flashes were sent through a slit to the polished face of the stellite block in the pendulum and back to an observing telescope.

In the course of the work it became necessary to observe at smaller amplitudes than was at first contemplated, and an increase in magnifying power seemed advisable. To obtain more light under these conditions a complex arrangement was tried containing a *KV610* neon-grid glow tube which carried a very heavy discharge. This proved unsatisfactory, apparently because of a pronounced and

[6] Monthly Notices of the Royal Astronomical Society **91**, 569-575 (March 1931).

variable after-glow amounting at times to several hundredths of a second. For this reason we returned to the use of the simple circuit containing a neon lamp, with which this effect appeared to be either negligibly small or nearly constant.

3. METHOD OF OBSERVING

For observing coincidences the telescope was provided with a micrometer eyepiece, the cross hairs of which could be set at the position at which coincidences took place. Because of a slight departure from symmetry in the setting of the photoelectric cell with respect to the clock pendulum, it usually happened that there would be a slight difference in the coincidence interval (and position) according as the end of a coincidence interval occurred during a downward or an upward motion of the flash. This variation was eliminated by using an even number of coincidence intervals for the calculation of the time of swing.

This method of observing enabled us to detect readily any irregularity in the action of the relay transmitting the signals. The flashes appeared alternately above and below the cross hairs of the microscope, gradually approaching the coincidence position. In our earlier work we attempted to use signals from a Riefler clock transmitted through a mechanical relay. The flashes, instead of approaching regularly the coincidence position, would frequently exhibit a retrograde motion. With the photoelectric outfit this was never noticed.

In changing the pendulum from the down to the up position it was rotated about its right and left axis, so that what was formerly the front side now became the back. The two positions of swing were denoted by the terms "front-down" and "back-up", respectively.

A typical example of the measurement of time of swing follows:

Pendulum no. 2. Front-down position. Pressure 0.04 mm of Hg; temperature $\begin{cases}23.6° \text{ C.}\\23.8° \text{ C.}\end{cases}$

Amplitude	Time	Coincidences	Interval
Radians			*Seconds*
0. 0047	8:22	8:35:03	449
. 0016	11:30	8:42:32	450
. 0011	12:30	8:50:02	
. 0009	1:00	(8 intervals)	449. 9
. 0007	1:30	9:50:01	
		(8 intervals)	450. 0
		10:50:01	
		(7 intervals)	450. 1
		11:42:32	
		(8 intervals)	450. 3
		12:42:34	
		(7 intervals)	449. 9
		1:35:03	453
		1:42:36	428
		1:50:04	

It will be noticed that the interval between coincidences is nearly constant except toward the end, where because of the small amplitude observing was more difficult. To obtain the mean interval the average of the first three times of coincidence was subtracted from the average of the last three, and the difference divided by the number of intervals represented.

Average of last three	13:42:34. 3
Average of first three	8:42:32. 3
	5:00:02. 0=18 002 seconds.

Dividing by 40 we obtain 450.05 seconds for the mean interval. This corresponds to a time of swing of 1.002 227 0 seconds.

The correction for temperature, by eq 5 is −0.000 000 8. The correction for arc, obtained by Borda's formula (U. S. Coast and Geodetic Survey, Special Publication No. 69, Modern Methods for Measuring the Intensity of Gravity, page 74) is −0.000 000 2. Applying these corrections we obtain for the time of swing 1.002 226 0 seconds at 20° C and zero amplitude.

The correction for clock rate was applied later in the computation of g.

4. CORRECTIONS

(a) CLOCK RATE

The Shortt clock was compared daily with the time signals from the U. S. Naval Observatory and with those from a crystal clock in the radio section of the National Bureau of Standards. The average daily rate of the Shortt clock was about −0.04 second over the period covered by the results given in this paper. During this period the rate was remarkably constant, its daily variation seldom reaching the second decimal place. While it is possible, as Loomis has shown, to obtain a much smaller rate from a Shortt clock this precision was ample for our requirements. Were this rate neglected altogether the error in the value of g would not exceed 1 part in a million.

(b) TEMPERATURE

The temperature of the pendulum was assumed to be that of the brass vacuum case, as measured by a thermometer on the outside of the case. After sealing the case the apparatus was allowed to stand overnight before observations were made.

In correcting the time of swing for temperature the values given in eq 5 and 6 for the down and up positions were used for pendulums with stellite blocks, and 0.000 000 3 for both positions of the all-silica pendulums.

(c) MOTION OF THE SUPPORT

Helmert (Beiträge, page 70) gives the mathematical theory of the effect of motion of the support on the time of swing of a pendulum, quoting an earlier investigation by C. S. Peirce, and confirming his result. If a pendulum of mass M swinging through an arc θ produces a horizontal elastic displacement of the support,

$$\sigma = \frac{Mgh\theta}{\epsilon l}$$

in which ϵ is an elastic constant. Helmert also finds the alteration in the equivalent length l of a simple seconds pendulum to be given by the equation:

$$l'=l\left(1+\frac{Mgh}{\epsilon l^2}\right)$$

From these two equations it follows that the apparent increase in the length of the pendulum

$$\delta l=l'-l=\frac{Mgh}{\epsilon l}=\frac{\sigma}{\theta}$$

or

$$\frac{\delta l}{l}=\frac{\sigma}{l\theta}$$

Since δl is very small compared to l, this is equivalent to saying that the pendulum may be regarded as oscillating about a new center elevated by δl above the moving axis of support.

The correction for the motion of the support thus requires a knowledge of the arc of swing and the displacement of the support. The displacement may be observed directly by an interferometer method, as is done by the U. S. Coast and Geodetic Survey, or may be calculated by its effect in producing motion in an auxiliary pendulum, as was done by the Potsdam observers. In the present work the interferometer method was employed. A small optically flat disk of fused silica was mounted by a little wax on one end of the knife-edge, which could be exposed for this purpose by moving the pendulums slightly to one side.

A specially built interferometer tube, carrying a second flat plate and a helium tube for illumination, was mounted on a support independent of the steel shelf that carried the pendulum case. The interferometer tube could be moved back and forth by a screw motion so that the two flat plates could be adjusted to give fringes.

In addition to testing the motion of the knife-edge itself, the test plate was mounted also on the steel strip which carried the knife-edge, and on the brass ring.

In these interferometer experiments a double-amplitude arc of swing of 0.06 radian was used instead of the smaller arc of 0.01 radian employed in time of swing measurements. With this large arc no motion of the brass ring was observable in any case.

When the test plate was mounted directly on the knife-edge there was, in most of the cases comprised in our results, no shift perceptible. In a few cases there was a slight motion, but this never exceeded one-tenth of a fringe. With a wave length of 0.6 μ an observed shift of 0.1 fringe corresponds to a motion of the test plate of 0.03 μ, which gives for the correction to the pendulum length

$$\delta l=\frac{\sigma}{\theta}=\frac{0.03\ \mu}{0.06}=0.5\ \mu$$

a maximum error of 1 part in 2 million.

(d) DAMPING

There are two sources of damping to be recognized in pendulum work. The first arises from the surrounding air and the second from friction at the knife-edge. These may be distinguished by the fact

that air friction, at the velocities to be encountered in a seconds pendulum, may be considered as proportional to the velocity, and that therefore the amplitude will decrease as an exponential function of the time, while damping due to friction at the knife-edge can not be expected to follow any such simple mathematical law.

An examination of the amplitude-time curves for our pendulums shows that the curves are closely exponential throughout. We may therefore conclude that the air damping is the principal factor to be considered, and that knife-edge friction is negligibly small in comparison.

The most accurate test of this point is furnished by swings through large amplitudes. An example of such a swing follows:

Pendulum no. 4. Up position. Stellite knife-edge and plane. Pressure (mm of Hg) $\begin{cases}0.05\\0.04\end{cases}$; temperature $\begin{cases}21.5°\text{ C.}\\21.7°\text{ C.}\end{cases}$

Amplitude	Time	$A_t=A_0\epsilon^{-kt}$ / Δt	k
Radians		*Minutes*	
0. 0236	9:44		
		76	0. 0095
. 0115	11:00		
		64	. 0096
. 0062	12:04		
		84	. 0090
. 0029	1:28		

The period of a damped vibration, where the damping effect is assumed proportional to the velocity is

$$T=\frac{\pi}{\sqrt{\frac{g}{l}-b^2}}=\pi\sqrt{\frac{l}{g}}\left[1+\frac{b^2l}{2g}+\ldots\ldots\right]\ldots\ldots \qquad (7)$$

in which

$$b=\frac{1}{nT}\log_\epsilon\left(\frac{\alpha_o}{\alpha_n}\right)$$

n=total number of swings.
α_o=initial amplitude.
α_n=final amplitude.

The shortest duration of swinging with any of our pendulums was about 3 hours, or 10,800 seconds. The ratio α_o/α_n was usually about 10. Since T is very nearly 1 second, these figures give $b=0.000\ 21$ and $b^2=0.000\ 000\ 04$. Taking $l=100$ and $g=980$ the corrective term $\frac{b^2l}{2g}=0.000\ 000\ 002$, a negligible amount.

(e) RESIDUAL AIR

In addition to contributing to the damping effect discussed in the preceding section, the surrounding air gives rise to another effect resulting jointly from hydrodynamic loading and from buoyancy.

By hydrodynamic loading there is an apparent increase in the inertia of the pendulum, and because of buoyancy there is an apparent diminution in weight. Both factors increase the time of swing.

This correction is best handled experimentally. Pendulum no. 1, the smallest and lightest of the set, was swung in air at different pressures in both the up and down positions with the following results:

Pressure	Time of swing	
	Up	Down
mm of Hg	*Seconds*	*Seconds*
0. 1	1. 0029	1. 0029
100	1. 0032	1. 0032
425	1. 0040	1. 0042
760	1. 0047	1. 0050

These results are represented graphically in figure 10.

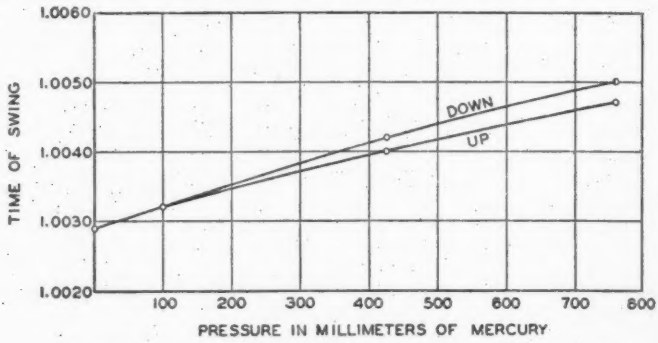

FIGURE 10.—*Relation between pressure and time of swing.*

It will be seen that both curves are sufficiently linear to enable us to calculate that the difference of time to be expected between the pressure at which the pendulum was usually swung (less than 0.1 mm) and a perfect vacuum is only 0.000 000 3 second, a negligible amount.

(f) COMPRESSIBILITY OF THE PENDULUM

It was suggested to us by Dr. C. Moon of our staff that consideration should be given to the question of a possible change in dimensions of the pendulum arising from the difference in pressure at which its length was measured and that at which its time of swing was determined.

The compressibility of fused silica has been determined to be about 3.1×10^{-6} per megadyne/cm^2.[7] Assuming the material isotropic, we may take one-third of this as the linear change. In consequence, the length in a vacuum may be expected to be greater than that in air by about 1 part per million.

The compressibility of brass is about one-fourth that of fused silica, hence such a correction would not be likely to arise with metal pendulums.

To test this point experimentally a brass tube was provided, large enough to hold the no. 2 pendulum. The ends were closed airtight, and windows were provided through which the length of the pendulum

[7] Adams, Williamson, and Johnston, J. Am. Chem. Soc. 41, 39 (1919).

could be measured. Measurements were taken with the tube alternately filled with air and evacuated to a pressure less than 5 mm.

The precision of the measurements was such that a change of 1 μ could be safely recognized, but fractions of a micron were uncertain. As a mean of over a hundred measurements it appeared that there was a slight elongation of the pendulum in the vacuum, certainly less than 1 μ, and apparently of the order of 0.5 μ.

The figure quoted for the compressibility of silica would indicate a change of about 1 μ, but it is to be remembered that this figure was obtained at very high pressures. It is quite probable that the compressibility at 1 atmosphere may be less. However, a correction of the order indicated, 0.5 μ, is too small to be certain of with the precision of our length measurements, and in any case would influence the value of g by less than 1 part in a million. It may therefore be neglected.

(g) FLEXURE OF THE PENDULUM

As a pendulum swings, it bends slightly, and from purely geometrical considerations its mean length and time of swing should be less than with a perfectly rigid pendulum. Calculation of the difference between the arc and the chord shows, however, that such an effect, with pendulums of the rigidity usually employed, is negligible.

Experimentally, it is found that there is a rather large effect of flexibility on time of swing resulting from bending stresses in the opposite direction from that indicated above, increased flexibility giving a greater time of swing. This effect is present in both the up and the down positions, and partly cancels out in applying eq 1.

This is illustrated by some preliminary experiments of ours with a pendulum composed for the most part of a strip of brass 37 mm wide and 3 mm thick. The pendulum carried two planes and could be swung on a fixed knife-edge, either in the plane of the strip or perpendicular to it. This amounted to swinging two pendulums differing greatly in flexibility. Because of its slightly greater moment of inertia the rigid pendulum should have the greater time of swing. Experiment, however, shows the reverse.

In table 2 is given a summary of the mean results obtained, illustrating how large this effect may be in an extreme case. The value of τ is calculated by the eq. 1.

TABLE 2.—*Time of swing of rigid and flexible pendulums*

Rigid		Flexible	
Position	Time	Position	Time
Up	0.997 81	Up	1.002 73
Down	.999 32	Down	1.000 63
Mean	0.998 57	Mean	1.001 68
Difference of means	0.003 11		
τ (rigid) = 1.000 48		τ (flexible) = 0.999 01	
Difference	0.001 47		

It will be seen in this table that the unreduced times differ in the mean by 0.003 11 second. By applying eq 1 this difference does not disappear, but is reduced to about half its value.

Any resultant flexure effect, if at all appreciable, should be most in evidence in the most flexible pendulums. For this reason several pendulums of different flexibilities were used by us.

The Potsdam investigators developed, on theoretical considerations, a formula for the flexure correction, which has been applied to our pendulums by Dr. H. L. Dryden of the National Bureau of Standards. The corrections in the value of g found by this formula are given in table 3 in parts per million.

TABLE 3.—*Flexure corrections to the value of g*

Pendulum number	Correction (units of the third decimal place)
2	−7
6	−5
4	−2

(h) AMPLITUDE

The theoretical correction for the effect of finite amplitude on the time of swing is given by the formula

$$T = T_0\left(1+\frac{\alpha^2}{16}+ \ldots\ldots\right)\ldots\ldots \quad (8)$$

LeRolland [8] found that this formula does not give the entire effect of amplitude upon period, but that, generally speaking, the values of the time of swing at different amplitudes on being thus reduced to zero amplitude still showed a decrease with diminishing amplitude.

Our experience confirms that of LeRolland. The Potsdam observers, probably because of the very small amplitudes at which they worked (from 30′ down), found that this effect was not strongly marked. The explanation of this discrepancy is doubtless connected with the effect of imperfection in the knife edge, which we have found to be the most serious difficulty with which we have had to deal, and which will be discussed at length in the next section. To avoid as far as possible the difficulty arising from the lack of applicability of eq 1 we finally limited the amplitude of swing of the pendulums to a maximum of about 30′ and made observations down to about one-twentieth of this value.

(i) IMPERFECTIONS OF THE KNIFE-EDGE

Not all materials are suitable for knife-edges. The conditions under which a knife-edge is expected to stand up are extreme. The area of contact with the supporting plane is so small that the pressure may be of the order of several tons per square centimeter. Moreover, this pressure, as the pendulum swings, is exerted alternately on one side or the other of the knife-edge, an alteration repeated each

[8] Annales Phys. 22, p. 236 and following (1922).

second for hours at a time, and a certain measure of fatigue of the edge (or the plane) may result. If under these conditions there should result a microscopic breakdown at any point of the edge, there may be quite a noticeable effect on the motion of the pendulum.

On one occasion we were fortunate enough to observe what was undoubtedly the result of such a breakdown. The knife-edge, of stainless steel, was working against a plane of fused silica, and observations were being made for damping. The results in table 4 were obtained.

TABLE 4.—*Observations for damping*

Time	Amplitude	Ratio of amplitudes
	mm	
10:53:30	31.69	----------
11:01:20	30.66	1.03
11:09:10	22.84	1.34
11:16:40	21.14	1.08

For the rest of the run (about 2 hours) the amplitude ratio varied between 1.08 and 1.10. It seems likely that at some time between 11:01 and 11:09 a breakdown occurred, requiring for the moment an extra expenditure of energy on the part of the pendulum, and leaving the edge in a condition which gave rise to slightly more friction than its initial condition.

Several such instances were noticed with knife-edges of different materials. The breakdown must have been very small, as in no case could we be certain of detecting anything by microscopic examination.

It is easily seen that a knife-edge may, for this reason, be too sharp. In fact, on a mathematically sharp edge any finite weight, however small, would produce an infinite pressure and an instant breakdown.

This being the case, why not use a cylindrical rod instead of a knife-edge? Experiments of this nature were made some 50 years ago by the U. S. Coast and Geodetic Survey,[9] but the results were not encouraging. Our experience has been similar. With too great a radius of curvature the damping becomes excessive, and the coincidence intervals show large variations.

As an instance of this, an agate knife-edge with a radius of about 10 μ was placed in service with a pendulum containing stellite blocks. The results were at first quite concordant, but after about a month's daily use the values of g began to show a steady progression downwards. A remeasurement of the radius gave 18 μ at one end of the knife-edge and 69 μ at the other.

An attempt was made to grind this edge to a uniform though larger radius by giving it a few strokes with a piece of thin aluminum foil charged with a fine abrasive, the strokes being directed perpendicularly to the edge and the foil being held so as to form an inverted V over the edge. As a grinding operation, this may perhaps be called successful, as the radius afterward measured 195 μ and 230 μ at its two ends. No apparent increase in width at the edge was noticeable.

The service results with this reground edge were very unsatisfactory. The damping was increased so that the duration of the swinging

[9] U. S. Coast and Geodetic Survey, Special Publication no. 69, Modern Methods for Measuring the Intensity of Gravity, page 14 (1921).

of the pendulum was reduced from its normal value of 6 hours to about 4½ hours. In addition, the coincidence intervals varied greatly, fluctuating by as much as 1 minute in an interval of about 18 minutes, whereas with a sharp edge this variation was usually but a few seconds. A similar behavior was noticed when the pendulum rolled by means of its stellite block on a support made of 1-mm steel drill rod.

The disturbing effect of too blunt a support is probably due to adhesion at the surface of contact under the great pressure existing there. As the pendulum swings this adhesion is being continually formed and broken loose, and this latter operation requires an expenditure of force, which over a larger area may show a greater variation than with a sharper pendulum and a consequently smaller area of contact.

But if a knife-edge may be too blunt as well as too sharp, what may be regarded as an optimum radius of curvatures? The answer to this must be expected to depend upon the material. Another agate edge, with a radius of about 35 μ, gave what we considered at that time satisfactory service for nearly 2 years, after which variable results began to make their appearance. On remeasurement the radius was then found to be 70 μ at one end and 165 μ at the other.

It is an obvious suggestion that the edge be kept sharp by regrinding. This is not a simple matter with agate, but is readily and quickly done with metallic edges. An edge of stellite with a radius of about 10 μ was found to have increased to 15 μ after 2 weeks' daily use. The procedure was then adopted of resharpening this edge after every three swings of the pendulum (in the up-down-up positions). By this procedure a radius of about 10 μ could be maintained, and the average departure from the mean of the values of g could be limited to a figure less than that attainable with any materials previously used.

The effects of use seem to be confined entirely to the knife-edge, the mirror surface of the optically flat planes showing no deterioration after several years in service.

LeRolland's experience [10] was that, generally speaking, the harder materials used for the edge and plane introduced the least irregularity in its time of swing. This agrees with our experience. But hardness is not the only quality necessary. A substance may be hard and very brittle, like fused silica, and an edge of this material showed itself to be inferior to one of agate, of the same chemical composition but of a different structure. A hard and tough material, such as stellite, gave better results than agate.

Still better results were obtained by the use of a special steel known as Halcomb chrome steel, of the following analysis:

C=0.96%
Mn=0.35
P=0.014
S=0.017
Si=0.25
Cr=1.31

An edge made of this steel, oil hardened at 950° C, and used against a stellite plane, gave us our best results. The scleroscope hardness of this edge measured from 86 to 90, while the similar figure for the stellite plane was from 76 to 83.

[10] Annales Phys. 22, 244 (1922).

VI. RESULTS

The best results were obtained with a knife-edge of the chrome steel mentioned in the last section. As will be seen by the tabulated results, the knife-edge appears to be a more important factor than the plane.

The measure of precision adopted was the average departure from the mean. This we consider preferable to the least square probable error of the mean. No matter how widely the individual results may vary, the probable error of the mean approaches zero as the number of observations increases indefinitely, and this may be misleading. On the other hand, as the number of observations is increased, the cumulative mean and the average departure from the mean both approach constancy. When this has been attained sufficiently for the purpose in hand there is nothing to be gained by taking additional observations.

In the following tables the results of our observations with the different combinations of planes and knife-edges are given in detail:

TABLE 5.—*Values of g*

Pendulum no. 3. Steel knife-edge. Stellite planes. Mass=3.6 kg. Relative flexibility (see table 1) 0.61.

Length at 20° C:

October 11, 1934 ..... 997.760 mm. h_1=695.3 mm.
November 22, 1934 ..... 997.759 mm. h_2=302.5 mm.
May 22, 1935 ..... 997.761 mm.

Mean ..... 997.760 mm.

Date, 1935	Pressure	Temperature	Amplitude	Time of swing (reduced to 20° C)		g	Cumulative mean
				Down	Up		
May	mm Hg	°C	*Radians*				
4	0.04-.06	22.6	0.0040-.0015		1.002 673 2		
6	.04-.06	22.2-22.4	.0046-.0009	1.002 504 2		980.090	980.090
7	.04-.08	22.5	.0045-.0007		1.002 672 4	092	091
8	.04-.08	22.2-22.4	.0050-.0009	1.002 502 6		091	091
9	.04-.08	22.7-22.4	.0045-.0009		1.002 670 4	088	090
10	.04-.08	22.3-22.6	.0061-.0011	1.002 504 8		083	089
11	.04-.07	22.6	.0040-.0014		1.002 667 7	082	088
13	.04-.10	22.3-22.5	.0059-.0006	1.002 503 6		083	087
14	.04-.08	22.8-22.7	.0045-.0009		1.002 666 4	086	086
15	.04-.06	22.5-22.7	.0051-.0009	1.002 501 5		089	087
16	.04-.10	22.8-22.7	.0050-.0009		1.002 665 4	087	087
17	.04-.06	22.4-22.6	.0067-.0010	1.002 502 3		084	087
18	.03-.06	22.3-22.8	.0055-.0006		1.002 663 5	084	087
20	.04-.06	22.3-22.4	.0051-.0007	1.002 510 6		084	086
21	.04-.08	22.5-22.7	.0045-.0007		1.002 662 8		

Mean value of g ..... 980.086 ±0.003 avg departure
Correction for clock rate ..... −0.001

980.085
Correction for flexure ..... −0.005

g=980.080 ±0.003 avg departure

During this work with pendulum no. 3 the knife-edge gave such consistent results that no resharpening was deemed necessary. Its radius of curvature, measured May 22, 1935, was 10 μ on one side of the center and 13 μ on the other. The knife-edge was then used with pendulum no. 4.

TABLE 6.—*Values of g*

Pendulum no. 4. Steel knife-edge. Stellite planes. Mass=3.5 kg. Relative flexibility (see table 1) 0.28.

Length at 20° C:

May 23, 1935 ..... 998.879 mm. h_1=698.0 mm.

June 17, 1935 ..... 998.880 mm. h_2=300.9 mm.

Mean ..... 998.879 mm.

Date, 1935	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
May	mm Hg	°C	*Radians*				
24	0.04–.08	22.2–22.3	0.0080–.0007		1.003 105 1		
25	.04–.07	22.5–22.8	.0040–.0004	1.003 009 6		980.085	980.085
27	.04–.06	22.2–22.5	.0073–.0006		1.003 100 9	082	084
28	.04–.08	22.7	.0045–.0004	1.003 009 3		084	084
29	.04–.08	22.5–22.6	.0084–.0006		1.003 101 9	082	083
31	.04–.08	22.5–22.8	.0085–.0005	1.003 010 8		080	083
June							
3	.04–.08	22.8	.0096–.0004		1.003 101 6	082	083
4	.04–.05	22.8	.0045–.0005	1.003 008 8		082	082
5	.04–.03	22.8–22.6	.0059–.0005		1.003 096 3	081	082
6	.04–.10	22.9–23.1	.0045–.0005	1.003 006 7		082	082
10	.05–.20	23.0	.0083–.0008		1.003 098 0	085	083
12	.03–.20	23.0–23.5	.0056–.0006	1.003 008 1		079	
13	.04–.09	23.4–23.7	.0050–.0005		1.003 090 5	076	
14	.03–.08	23.0–23.7	.0057–.0008	1.003 005 6		067	
15	.03–.06	23.5–23.6	.0050–.0007		1.003 082 5		

Mean value of g ..... 980.083 ±0.0014 avg departure

Correction for clock rate ..... −0.001

980.082

Correction for flexure ..... −0.002

g=980.080 ±0.0014 avg departure

It will be noticed that while up to June 10 the values of g had maintained a fairly constant level, a marked decrease occurred after that date. Regarding this as probably caused by a breakdown of the knife-edge, its radius of curvature was remeasured on June 17. The results on the two sides were 11 μ and 13 μ. If the falling off of the values of g was caused by a breakdown of the knife-edge, such a deterioration must have been on a scale too small for measurement. The knife edge was resharpened and remeasured, giving 4 μ at each end. This, by the way, is the value that we have found for the radius of curvature of a razor blade. The resharpened knife-edge was set up with pendulum no. 2, and it was interesting to see that the results for g returned to their normal value.

TABLE 7.—*Values of g*

Pendulum no. 2. Steel knife-edge. Stellite planes. Mass=1.9 kg. Relative flexibility (see table 1) 0.89.
Length at 20° C:
June 18, 1935 ..... 997.418 mm. h_1=709.1 mm.
July 5, 1935 ..... 997.418 mm. h_2=288.3 mm.
Mean ..... 997.418 mm.

Date, 1935	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
June	mm Hg	°C	*Radians*				
19	0.04	23.2–23.4	0.0062–.0008		1.002 288 4		
20	0.03–.04	23.4	.0070–.0007	1.002 237 4		980.084	980.08
21	.03–.10	23.2–23.7	.0055–.0006		1.002 279 1	084	084
22	.03–.04	23.6–23.8	.0045–.0009	1.002 233 8		084	084
24	.03–.07	23.0–23.2	.0057–.0007		1.002 275 0	092	086
25	0.03	23.4–23.3	.0045–.0006	1.002 229 2		093	087
26	.03–.04	23.0	.0074–.0008		1.002 266 3	087	087
27	0.04	23.4–23.6	.0050–.0007	1.002 229 7		079	086
28	.03–.04	23.4	.0058–.0006		1.002 254 4	073	085
29	0.04	23.8	.0035–.0011	1.002 227 6		081	084
July							
1	.03–.06	23.3–23.8	.0036–.0008		1.002 260 8	088	085
2	0.04	23.6–23.8	.0047–.0007	1.002 226 1		089	085
3	.03–.04	23.4–23.6	.0048–.0006		1.002 258 2		

Mean value of g ..... 980.085 ±0.0045 avg departure
Correction for clock rate ..... +0.001
980.086
Correction for flexure ..... −0.007
g=980.079 ±0.0045 avg departure

TABLE 8.—*Values of g*

Pendulum no. 4. Steel knife-edge. Fused-silica planes. Mass=3.6 kg. Relative flexibility (see table 1) 0.28. Length at 20° C:
March 19, 1935 ..... 998.730 mm h_1=707.7 mm.
h_2=291.0 mm.

Date, 1935	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
April	mm Hg	°C	*Radians*				
20	0.04–.06	21.9–21.8	0.0055–.0007		1.002 977 3		
22	.04–.06	21.6–21.8	.0062–.0005	1.002 912 2		980.079	980.079
23	.04–.09	21.9–21.8	.0050–.0006		1.002 976 4	079	079
24	.04–.06	21.7–22.0	.0063–.0005	1.002 912 4		081	080
26	.04–.06	22.0	.0059–.0006		1.002 980 1	082	080
29	.04–.06	22.0–22.2	.0070–.0004	1.002 913 2		075	079
30	.04–.05	22.2–22.3	.0047–.0005		1.002 972 3	071	078
May							
1	.04–.08	22.1–22.2	.0065–.0005	1.002 912 2		078	078
2	.04–.06	22.4–22.6	.0050–.0007		1.002 979 2	081	078
3	.04–.07	22.3–22.4	.0061–.0004	1.002 913 1			

Mean value of g ..... 980.078 ±0.003 avg departure
Correction for clock rate ..... −0.001
980.077
Correction for flexure ..... −0.002
g=980.075 ±0.003 avg departure

The results in tables 5 to 8 are the best that we have obtained, as measured by the small total spread of the individual values of g and the average departure from the mean. It should be noted that these results were all obtained with a chrome steel knife-edge and planes of stellite or fused silica. The results in the tables that follow were obtained with the same planes but different materials in the knife-edge, and it is of interest to see the marked deterioration in the quality of the results as compared with those in the preceding tables. These later results are not of importance as contributions to the final result, but are given because they show that the material of the knife-edge is of prime importance and that of the planes is secondary.

In some cases, as in tables 9 and 10, it was found necessary to resharpen the knife-edge (stellite) after every third determination of time of swing in order to keep the variation of the values of g within tolerable bounds. In such cases the value of g was calculated from those times of swing which formed a triplet uninterrupted by a sharpening of the knife-edge.

In none of the tables have results been suppressed because of their wide departure from the mean.

TABLE 9.—*Values of g*

Pendulum no. 2. Stellite knife-edge. Stellite plane. Mass=1.9 kg. Relative flexibility (see table 1) 0.89. Length at 20° C:

July 25, 1934	997.415 mm.	h_1=709.1 mm.
Oct. 8, 1934	997.417 mm.	
Mean	997.416 mm.	h_2=288.3 mm.

Date, 1934	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
Sept.	mm Hg	°C	*Radians*				
7	0.04	22.8–23.0	0.0069–.0009		1.002 284 4		
8	.04	23.1	.0050–.0012	1.002 230 3		980.100	980.100
10	.04	22.8–23.0	.0071–.0007		1.002 274 9		
11	.04	23.0	.0050–.0012	1.002 237 8			
12	.04	22.9–23.0	.0057–.0011		1.002 274 7	095	098
13	.04	23.0	.0053–.0009	1.002 222 5			
15	.04	23.1	.0054–.0011		1.002 213 4		
17	.04	22.8	.0070–.0009	1.002 217 9		081	092
18	.04	22.8	.0050–.0010		1.002 256 1		
19	.04	22.2–22.7	.0078–.0011		1.002 278 2		
20	.04	22.9	.0050–.0012	1.002 232 3		081	090
21	.04	22.7–22.8	.0059–.0008		1.002 263 3		
22	.04	23.0–22.8	.0050–.0014		1.002 277 6		
24	.04	22.8–22.9	.0059–.0009	1.002 231 3		092	090
25	.04	22.9–23.0	.0050–.0009		1.002 273 9		
26	.04	22.8–23.0	.0069–.0015		1.002 285 4		
27	.04	23.0	.0043–.0009	1.002 235 2		084	089
28	0.04–0.07	22.8	.0054–.0009		1.002 275 3		
29	.04	23.0–23.2	.0062–.0010		1.002 282 5		
Oct.							
1	.04	22.6–23.5	.0059–.0012	1.002 233 6		082	088
2	0.04–0.07	22.5–22.7	.0057–.0008		1.002 267 7		
4	.04	22.4–22.7	.0047–.0009		1.002 278 7		
5	.04	22.2–22.5	.0058–.0008	1.002 236 3		076	088
6	.04	22.5–22.7	.0046–.0012		1.002 273 9		

Mean value of g ..... 980.086±0.007 avg. departure
Correction for clock rate, zero.
Correction for flexure ..... −0.005

g=980.081±0.007 avg. departure

TABLE 10.—*Values of g*

Pendulum no. 3. Stellite knife-edge. Stellite plane. Mass=3.6 kg. Relative flexibility (see table 1) 0.61. Length at 20° C:

Oct. 11, 1934 ..... 997.760 mm. h_1=695.3 mm.
Nov. 22, 1934 ..... 997.759 mm.

h_2=302.5 mm.

Adopted value ..... 997.760 mm.

Date, 1934	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
Oct.	mm Hg	° C	*Radians*				
12	0.04	22.5–22.7	0.0063–.0012		1.002 671 6		
15	0.04–0.40	21.9–22.1	.0048–.0011	1.002 496 7		980.110	980.110
16	.04	22.2–22.1	.0050–.0011		1.002 665 4		
17	.04	22.1–22.3	.0062–.0013		1.002 671 9		
18	0.04–0.20	22.3–22.5	.0047–.0009	1.002 503 1		088	099
19	.04	22.0–22.3	.0055–.0011		1.002 664 8		
22	.04	22.2–22.4	.0058–.0012		1.002 677 7		
23	.04	22.3–22.5	.0054–.0010	1.002 506 4		081	093
25	0.04–0.05	22.6–22.7	.0052–.0011		1.002 665 6		
26	.04	22.5–22.7	.0049–.0012		1.002 670 9		
27	.04	22.5–22.8	.0069–.0013	1.002 506 7		080	090
29	.04	21.8–22.0	.0060–.0016		1.002 672 3		
30	0.03–0.04	22.0	.0058–.0007		1.002 652 5		
31	.04	22.0–22.2	.0067–.0014	1.002 503 8		056	
Nov.							
1	.04	22.1–22.2	.0050–.0012		1.002 645 6		
2	.04	22.0–22.1	.0055–.0011		1.002 675 4		
5	.04	22.0–22.1	.0055–.0012	1.002 507 0		081	083
6	.04	22.0–22.2	.0050–.0011		1.002 670 5		
7	0.04–0.06	22.0–22.1	.0060–.0010		1.002 677 5		
8	.04	22.1–22.2	.0049–.0009	1.002 502 7		098	085
9	.04	22.0–22.2	.0054–.0012		1.002 672 0		
12	.04	21.2–21.8	.0056–.0012		1.002 671 9		
14	.04	21.3–21.4	.0056–.0011	1.002 506 4		080	084
15	.04	21.0–21.4	.0059–.0011		1.002 670 4		
16	.04	21.2–21.4	.0054–.0011		1.002 664 3		
19	.04	21.4–21.6	.0061–.0011	1.002 502 3		067	082
20	.04	21.6–21.9	.0057–.0012		1.002 641 4		

Mean value of g ..... 980.082±0.011 avg. departure
Correction for clock rate, zero.
Correction for flexure ..... —0.005

g=980.077±0.011 avg. departure

The results in table 12 are of interest only as an illustration of the inferiority of agate to chrome steel or even to stellite as a knife-edge material. The results of this series are better than those of a number of similar cases that might be cited. It will be noted that the results given in tables 11 and 12 were obtained within a month of each other, with the same pendulum, the only difference being the change from stellite to agate in the knife-edge.

TABLE 11.—*Values of g*

Pendulum no. 4. Stellite knife-edge. Stellite plane. Mass = 3.5 kg. Relative flexibility (see table 1) 0.28. Length at 20° C:

July 28, 1933	998.818 mm.	h_1=698.8 mm.
Sept. 19, 1933	998.820 mm.	
Jan. 22, 1934	998.817 mm.	h_2=300.0 mm.
June 1, 1934	998.818 mm.	
Adopted value	998.818 mm.	

Date, 1935	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
May	mm Hg	°C	*Radians*				
9	0.04	21.9–22.0	0.0040–.0004		1.003 137 3		
10	.03	22.0–21.9	.0036–.0004	1.003 055 7		980.089	980.089
11	.04	22.4–22.1	.0039–.0004		1.003 138 9	097	094
12	0.03–0.04	21.8–21.9	.0041–.0004	1.003 001 7		100	096
15	0.06–0.03	22.1–22.2	.0043–.0004		1.003 133 0	102	097
16	.03	21.9	.0029–.0003	1.002 996 5		111	100
17	0.09–0.04	22.2–22.0	.0046–.0004		1.003 129 7	111	102
19	.04	22.2	.0032–.3003	1.002 994 7		102	102
21	.03	22.0–22.1	.0044–.0003		1.003 113 2	083	100
22	.04	22.3	.0042–.0004	1.002 998 4		077	098
23	.03	22.1	.0039–.0003		1.003 112 7	070	095
25	.03	22.0–22.2	.0038–.0003	1.003 002 5		069	092
26	.04	22.4–22.1	.0044–.0004		1.003 121 9		

Mean value of g ..... 980.092±0.013 avg. departure
Correction for clock rate, zero
Correction for flexure ..... −0.002

g=980.090±0.013 avg. departure

TABLE 12.—*Values of g*

Pendulum no. 4. Agate knife-edge. Stellite plane. Mass = 3.5 kg. Relative flexibility (see table 1) 0.28. Length at 20° C:

July 28, 1933	998.818 mm.	h_1=698.8 mm.
Sept. 19, 1933	998.820 mm.	
Jan. 22, 1934	998.817 mm.	h_2=300.0 mm.
June 1, 1934	998.818 mm.	
Adopted value	998.818 mm.	

Date, 1934	Pressure	Temperature	Amplitude	Times of swing (20° C)		g	Cumulative mean
				Down	Up		
May	mm Hg	°C	*Radians*				
29	0.03–0.04	22.0–22.1	0.0048–.0003	1.002 913 2			
31	.03–0.04	22.2–22.0	.0047–.0004		1.002 913 5	980.078	980.078
June							
1	0.04	22.1	.0039–.0004	1.002 911 5		084	081
2	.03–0.04	22.1–22.4	.0042–.0004		1.002 918 2	085	082
4	.03–0.04	22.0–22.5	.0042–.0003	1.002 912 6		056	076
5	.04–0.05	22.2–22.5	.0043–.0004		1.002 879 6	037	068
6	.03–0.04	22.2–22.6	.0045–.0003	1.002 917 2		048	065
7	0.04	22.8–22.7	.0040–.0004		1.002 928 5	089	068
8	.03–0.04	22.2–22.5	.0047–.0004		1.002 936 4		
9	0.04	22.8	.0042–.0005	1.002 917 6			
11	.03–0.04	22.4–22.7	.0034–.0003		1.002 946 8	070	068
14	.05–0.04	23–0–22.8	.0038–.0003		1.002 872 0		
15	0.04	22.8	.0041–.0005	1.002 908 7			

Mean value of g ..... 980.068 ± 0.018 avg. departure
Correction for clock rate, zero.
Correction for flexure ..... −0.002

g=980.066 ± 0.018 avg. departure

TABLE 13.—*Summary of values of g*

Pendulum number	2	3	4
Relative flexibility	0.89	0.61	0.28
Stellite plane Steel knife-edge	980.079 ±0.0045	980.080 ±0.003	980.080 ±0.0014
Fused-silica plane Steel knife-edge			980.075 ±0.003
Stellite plane Stellite knife-edge	980.081 ±0.007	980.077 ±0.011	980.090 ±0.013
Stellite plane Agate knife-edge			980.066 ±0.018

In connection with table 13 the following points may be noted:

1. The values of *g* obtained with the steel knife-edge (rows 1 and 2, table 13) show the greatest precision, the total spread of the individual values being 0.022 and the average departure from the mean less than 0.005.

2. A change in the material of the plane from stellite to fused silica (the knife-edge remaining the same) makes no change in the order of precision.

3. A change in the material of the knife-edge from steel to stellite (row 3) reduces the precision considerably, the average departure becoming of the order 0.01 and the spread of the individual values 0.055.

4. It will be noticed that in some cases (table 7) there is a tendency to a small but steady decrease in the times of swing, while the value of *g* remains fairly constant. This may be due to a slight progressive wear of the knife-edge, the effect nearly cancelling out in the application of eq 1.

The mean of the four best results (rows 1 and 2), weighted inversely as their average departures, is 980.079. If we include the three second-best results (row 3) the mean is 980.080 ±0.003.[11] But since even with the four best results the spread of the individual values is 0.022 and the average departure of a set may be as much as 0.0045, it is our feeling that

g=980.08 cm sec^{-2}±0.003 average departure

goes as far in accuracy as is reasonably certain.

It should be noted that this result involves 70 single determinations of *g*.

The geographical coordinates of this gravity station, determined from information furnished by the U. S. Coast and Geodetic Survey, are as follows:

Latitude	38°56′30.143″ N.
Longitude	77°03′56.893″ W.
Elevation above sea level	94.75 meters.

It may be of assistance in appraising the precision of the foregoing result to summarize the various minor sources of error for which no correction was deemed necessary. These are given in table 14.

[11] Our earlier results, obtained with knife-edges of agate and fused silica, are of too poor a grade to be considered for inclusion in the final result. Table 12 gives an example of perhaps the most presentable of these results

TABLE 14.—*Effect of minor sources of error*

Source	Estimated effect on g
Position of knife-edge on plane	Maximum not known. Minimum less than 1 part per million.
Parallelism of plane	1×10^{-8}.
Equality of T_1 and T_2	$<1.2\times10^{-7}$.
Center of gravity in line of supports	2×10^{-8}.
Departure of knife-edge from level	5×10^{-7}.
Error of standard scale	$\geqslant1\times10^{-6}$.
Elastic deformation of pendulum under own weight	$\geqslant1\times10^{-6}$.
Microscope error	$<1\times10^{-6}$.
Clock-rate variation	$<1\times10^{-6}$.
Motion of support	5×10^{-7}.
Damping	2×10^{-9}.
Compressibility of pendulum	5×10^{-7}.

VII. THE POTSDAM DETERMINATION

The value of g in the pendulum room at the National Bureau of Standards, as deduced from the direct connection made with Potsdam to the pendulum room in 1933 by Lt. Brown of the U. S. Coast and Geodetic Survey, is 980.100. The value adopted as the result of our absolute measurement is 980.08. The difference, 2 parts in 100 000, suggests that an examination of possible causes is desirable. In this connection it should be remembered that the various connections between Washington and Potsdam have differed by as much as 9 parts in a million.

The precision claimed in the Potsdam report is ±0.003. It is to be noted that this is a least square probable error, and corresponds to a much larger average departure from the mean.

The Potsdam results are tabulated and discussed as the length of the equivalent simple seconds pendulum, and reduced to the value of g only at the end of the report after all reductions had been made. We shall find it convenient, however, to quote the Potsdam results translated into equivalent values of g at the National Bureau of Standards in Washington, using for this purpose the difference found by Lt. Brown:

$$\text{Potsdam}-\text{Washington}=+1.174.$$

The Potsdam results fall into two classes, those obtained with pendulums carrying two knife-edges and those given by pendulums provided with two planes. In the first class there are given 108 separate values and in the second class 84. The maximum, minimum and mean values are given in table 15.

TABLE 15.—*Values of g at Washington derived from Potsdam*

	Two knife-edges	Two planes
Maximum	980.180	980.136
Mean	980.090	980.072
Minimum	980.008	979.983
Total spread	0.172	0.153
Average departure from mean	0.017	0.026
Number of individual results	108	84

Different methods of classifying and weighting the subgroups of individual observations give mean values ranging from 980.082 to 980.089.

We may direct attention to the following points of interest in the above table.

1. The spread of the separate values is nearly 3 times that (0.055) obtained in the less accurate sets of our work. The average departure from the mean is also considerably greater than ours.

2. The 70 single observations in our work will therefore compare favorably with the greater number of observations of less precision in the Potsdam report.

3. The weighted mean of the Potsdam observations, obtained as above, is in reasonable agreement with our adopted result.

It remains to be explained how this Potsdam experimental mean was increased to give 980.100 at Washington.

It was recognized by the Potsdam observers that knife-edge errors played a large part in absolute-gravity work. A considerable portion of the Potsdam report is devoted to an attempt to evaluate these errors on the basis of the variations in the results given by the different pendulums employed. As a result of this evaluation the value of g was raised to 980.100 (at Washington). This process of correction appears to amount for the most part to an extrapolation of the results obtained with the different pendulums to that which would correspond to a pendulum of zero mass. The masses of the pendulums ranged from 2.86 to 6.23 kg, and in the extrapolation referred to the lightest pendulum seems to have had a disproportionate influence. Our results do not indicate a variation with mass, and therefore no such adjustment has been made.

WASHINGTON, July 29, 1935.

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BOILING-POINT–COMPOSITION DIAGRAM FOR DILUTE AQUEOUS SOLUTIONS OF DEUTERIUM OXIDE

By Edgar R. Smith and Mieczysław Wojciechowski [1]

ABSTRACT

The differences between the boiling points of dilute aqueous solutions of heavy water and the boiling point of ordinary water were measured in the range from 0.3 to 7 percent of D_2O. The boiling points were found to increase linearly with increase in D_2O, according to the equation mole % of $D_2O = 70.9\ (\Delta T)$, where ΔT is the boiling point in degrees centigrade minus 100. The measurements, made with ebulliometers of the type devised by W. Świętosławski, were found to offer a rapid method for the analysis of solutions of heavy water.

The differences between the boiling points and condensation temperatures of the same solutions were measured in a differential ebulliometer which gave a fractionation equivalent to about one theoretical plate. The small separation between the vapor and liquid lines on the boiling-point–composition diagram shows that the separation of heavy water by fractional distillation would require columns of extremely high efficiency.

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I. INTRODUCTION

It has been shown [6] [2] that the freezing points of mixtures of H_2O and D_2O can be expressed by the equation $t = 4.213x - 0.411x^2$, where t is the freezing point in degrees centigrade, and x is the mole fraction of D_2O. The solidus-liquidus curves nearly coincide, the maximum difference between them being 0.02° at about 42 percent of D_2O [2], so that very little separation can be effected by fractional crystallization [3]. On the other hand, it has been shown [4, 5, 7, 18] that an appreciable separation can be obtained by fractional distillation. While the electrolytic method of concentrating D_2O is economical and convenient in the last stages, a great deal of energy is required to electrolyze the large initial amount of water to a small volume. For this reason it appeared desirable to investigate the relation between the compositions of the liquid and vapor phases in equilibrium at the normal boiling points of mixtures of H_2O and D_2O in the dilute range, up to about 7 percent of D_2O.

[1] Guest worker from the Polytechnic Institute, Warsaw, Poland.
[2] The figures in brackets refer to references listed at the end of the paper.

II. MATERIALS AND METHOD

Five mixtures of H_2O and D_2O, containing approximately 0.3, 0.7, 1.0, 3.2, and 7.0 percent of D_2O, were prepared by electrolysis. These were purified by distillation from alkaline permanganate followed by simple distillation, with the rejection of equal initial and final portions. The density of each purified mixture was determined by the differential method of twin quartz pycnometers [14, 19] and the mole fraction x of D_2O in each was calculated from the equation $x=9.416\Delta S-1.00(\Delta S)^2$, where $\Delta S=S-1$, and S is the specific gravity of the mixture at 25°, compared with normal water at 25°. This equation was derived from that of Luten [9], $S=1.0000+0.1044x+0.0012x^2$, using the recent value of 1.1074 obtained by Tronstad, Nordhagen, and Brun [17], for the specific gravity of pure D_2O at 25°.

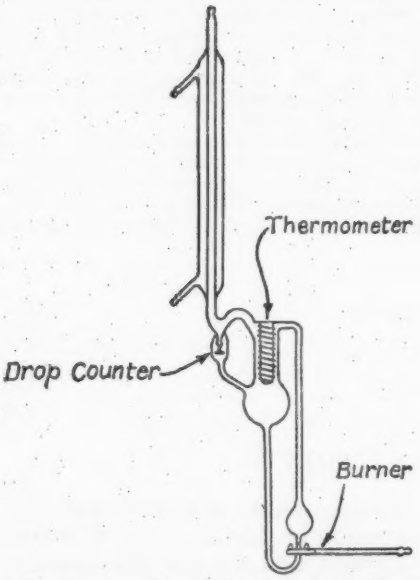

FIGURE 1.—*Simple barometric ebulliometer.*

For the determination of the boiling points of the mixtures, two identical simple barometric ebulliometers of the type developed by Świętosławski [15], shown in figure 1, were used.[3] One of these was filled with purified normal water, the other with the mixture to be investigated, and they were mounted side by side at the same level. Both waters were boiled continuously at the same rate, as measured by means of the drop counters below the condensers in the ebulliometers. The boiling points, measured as described below, were found to remain constant within wide limits of the rate of boiling, showing that superheating did not occur, so a convenient rate within these limits was adopted.

The difference between the boiling point of each mixture and that of normal water was determined in the following way. The resistance of a calibrated platinum-resistance thermometer (coiled-filament type) [10], immersed in the mercury-filled thermometer well of the ebulliometer containing normal water, was measured with a calibrated Mueller thermometer bridge. A stop watch was started and the thermometer was quickly transferred to the ebulliometer containing the mixture. After a 5-minute interval, the resistance of the thermometer in the mixture was measured and then the thermometer was quickly transferred back to the ebulliometer containing normal water. After another 5-minute interval the resistance of the thermometer at the boiling point of normal water was again measured, and the pro-

[3] The ebulliometers used in this work were made by Stefan Obojski, glassblower at the Polytechnic Institute, Warsaw, Poland, to conform to the specifications of W. Świętosławski.

cedure repeated to obtain a continuous series of 13 readings at equal time intervals. In this way, the average of each two successive measurements on normal water gave the value of the resistance which the thermometer would have had at the boiling point of normal water if measured at the same time and pressure as the intermediate measurement on the mixture. Ordinary variations which occur in atmospheric pressure make this procedure necessary for precise work since a change of only 0.03 mm in pressure changes the boiling point of water by 0.001° C, and in this work changes of less than 0.001° C were measured. To illustrate the procedure, the data obtained for the mixture containing 6.955 percent of D_2O are given in table 1.

TABLE 1.—*Data for mixture containing 6.995 mole % of* D_2O

Mixture	Resistance in international ohms			ΔT
	Individual readings	Average normal water	Average D_2O mixture	
				°C
Normal water	35. 20020			
D_2O mixture	35. 20990	35. 20018		0. 0972
Normal water	35. 20015		35. 20999	. 0984
D_2O mixture	35. 21008	35. 20030		. 0978
Normal water	35. 20045		35. 21024	. 0979
D_2O mixture	35. 21040	35. 20053		. 0997
Normal water	35. 20060		35. 21053	. 0993
D_2O mixture	35. 21065	35. 20074		. 0991
Normal water	35. 20088		35. 21070	. 0982
D_2O mixture	35. 21075	35. 20084		. 0991
Normal water	35. 20080		35. 21049	. 0969
D_2O mixture	35. 21023	35. 20080		. 0943
Normal water	35. 20080			

Average ΔT=0.0980 ±0.0011° C

Each measurement on normal water is also bracketed between two equally spaced measurements on the D_2O mixture, thus giving the series of differences in boiling points shown in column 5 of table 1. Within the precision of the differences measured, each 0.0001 ohm is equivalent to 0.001° for the thermometer used, so that the difference between the boiling point of the D_2O mixture and the boiling point of normal water under the same pressure is obtained by multiplying the difference in resistance by 10. From the measurements of Miles and Menzies [11] on the vapor pressure of pure deuterium water, it is certain that the ratio dT/dp for dilute aqueous solutions of D_2O is very close to the same ratio for ordinary water at 100°. Consequently the difference in boiling point found at the average pressure prevailing during the measurement (within 10 mm of normal) is the same, within the precision of the measurements, as the difference under normal pressure. The boiling point of water containing 6.955 mole percent of D_2O is therefore 100.098 ±0.001° C.

The difference between the boiling point and condensation temperature of each mixture was measured in a differential ebulliometer, of the type standardized by Świętosławski [15], shown in figure 2. The resistance of the thermometer was measured in the lower thermometer well, a stop watch was started and the thermometer quickly transferred to the upper well. After a 5-minute interval the resis-

tance of the thermometer in the upper well was measured and then the thermometer was transferred back to the lower well again. After another 5-minute interval the resistance at the boiling point was again measured, and the procedure was repeated to obtain a series of readings at equally spaced intervals of time. By this method differences due to changes in barometric pressure during the measurements were rendered negligible, as in the measurements of boiling point with the simple ebulliometers. The differential ebulliometer thus served as its own barometer. The precision obtained was first determined by using normal water in the differential ebulliometer and measuring 11 successive values of the difference between the boiling and condensation temperatures. The results showed that, within a few ten thousandths of 1°, there was no difference between these two temperatures in the case of ordinary water and, in addition, that equilibrium was obtained without superheating effects and that the water had been adequately purified.

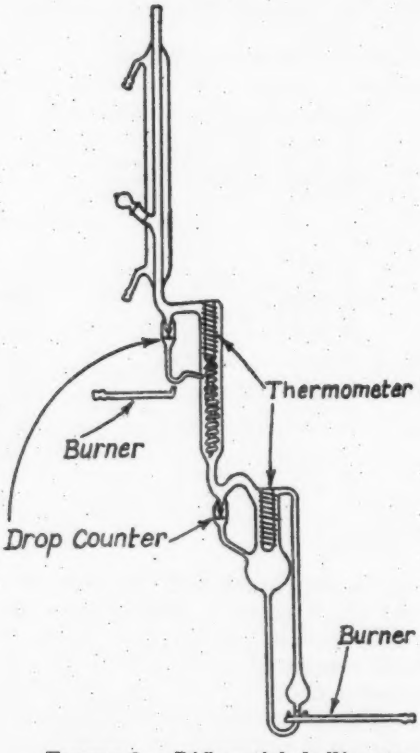

FIGURE 2.—*Differential ebulliometer.*

III. EXPERIMENTAL RESULTS AND CONCLUSIONS

In table 2 the values in the first column are the measured differences in density between the solutions and normal water, the second column shows the corresponding values of ΔS, the third contains the calculated mole percent of D_2O in each solution, the fourth gives the difference between the boiling point of each solution and the boiling point of normal water, as measured with the simple barometric ebulliometers, and the fifth column shows the difference between the boiling point of each solution and the temperature of condensation of its vapor in the differential ebulliometer.

To obtain the composition of the vapor in equilibrium with the boiling solution, the number of theoretical plates equivalent to the space between the thermometer wells in the differential ebulliometer, considered as a fractionating column, was determined. For this determinination two binary mixtures were used for which the boiling-point–composition data for the liquid and vapor phases seem to be well known. These were benzene-ethylene chloride [12, 13] and heptane-toluene [1], the data for the latter system being apparently more

TABLE 2.—*Boiling-point–composition data for dilute solutions of* D_2O

ΔD	$\Delta S = \frac{10^3 \Delta D}{0.99707}$	Mole % of D_2O	ΔT (bp−100°)	Δt (bp−*C. T.*)
ppm				
329	0.000330	0.311	0.0039	0.0014
720	.000722	.680	.0090	.0014
1,099	.001102	1.038	.0149	.0013
3,349	.003359	3.162	.0444	.0016
7,370	.007392	6.955	.0980	.0020
	(.1074)	(100.)	(1.40)	

consistent and reliable than those for the former. The method was to fill the differential ebulliometer with a mixture of known composition, measure the difference between the boiling point and condensation temperature, and from the known boiling-point–composition diagram for the system, to determine graphically the corresponding number of theoretical plates. The plate equivalent of the differential ebulliometer was found to be 0.90 with the benzene-ethylene chloride mixture and 0.96 with the heptane-toluene mixture. The value of slightly less than one theoretical plate indicates that although a temperature equilibrium, within a few hundredths of 1°, was attained between the boiling and condensation temperatures, the true composition equilibrium between the liquid and vapor phases was not attained, probably because of the rapid rate of boiling required to pump the mixture of liquid and vapor over the lower thermometer well (fig. 2). However, for the purpose of this investigation it is sufficiently accurate to consider the differential ebulliometer as equivalent to one theoretical plate.

The relation between normal boiling point and composition of the system H_2O–D_2O is shown graphically in figure 3. The boiling point increases linearly with increase in D_2O, the largest deviation of any point from the straight line labeled "liquid" being only a few ten-thousandths of 1°. This line is represented by the equation

$$\text{mole \% of } D_2O = 70.9\Delta T, \qquad (1)$$

in which ΔT is the increase in normal boiling point accompanying the increase in D_2O. The ease and rapidity with which comparisons of boiling points can be made with precision, by means of the ebulliometric technique of Świętosławski, suggests this method as a convenient analytical procedure for following the early stages in the production of heavy water. The linearity of the relation evidently extends through the entire range of composition since, by extrapolation of the straight line, or calculation from equation 1, a value of 101.41° C is obtained for the boiling point of pure D_2O as compared with 101.42° measured by Lewis and Macdonald [8], and 101.40± 0.016° C obtained by Miles and Menzies [11] from vapor-pressure measurements.

The curve labeled "vapor" in figure 3 shows the composition of the vapor in equilibrium with the boiling mixtures and is based on the value of 1 for the theoretical-plate equivalent of the differential ebulliometer. The closeness of the vapor and liquid composition lines indicates that a large number of theoretical plates would be required in a fractionating column to effect much separation.

Although the system consists of two components, H_2O and D_2O, there are in reality three substances present, because of the reaction

$$H_2O+D_2O=2\ HDO. \tag{2}$$

Topley and Eyring [16] have calculated the equilibrium constant K of this reaction to be 3.26, while the simple assumption of random distribution [7] gives 4 for the constant. In dilute solution the use of

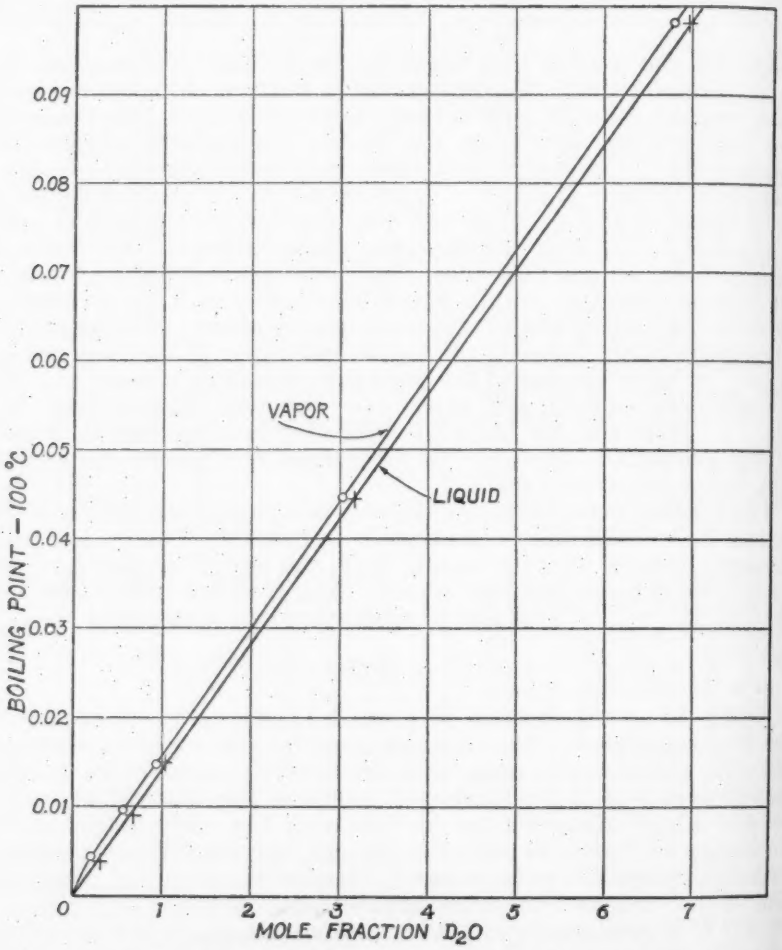

FIGURE 3.—*Boiling-point–composition diagram.*

either value gives practically the same result for the amount of HDO present. For example, in a mixture containing 1 percent of D_2O, the fraction of the D_2O converted to HDO is 0.985, if $K=3.26$ and 0.990 if $K=4$. For simplicity, without appreciably affecting the results, K will be assumed to be 4. On the basis of this value of K and the assumption that the vapor pressure of pure HDO is the geometric mean of the vapor pressures of H_2O and D_2O, i. e., $p_{HDO}=(p_{H_2O}p_{D_2O})^{1/2}$, it has been shown by Wynne-Jones [20] that, for ideal solutions, the

mole ratio of D to H in the liquid phase divided by the mole ratio of D to H in the vapor phase would be

$$R=(p_{H_2O}/p_{D_2O})^{1/2}. \quad (3)$$

Values of $(p_{H_2O}/p_{D_2O})^{1/2}$ corresponding to different temperatures can be computed by means of the equation

$$\log \frac{p_{D_2O}}{p_{H_2O}}=-16.998671+\frac{268.8426}{T}+7.4971604 \log T$$
$$-9.761107\times10^{-3}T+4.4288\times10^{-6}T^2 \quad (4)$$

obtained by Miles and Menzies [11] from comparative measurements of the vapor pressures of ordinary water and deuterium water in differential tensimeters. According to this equation $(p_{H_2O}/p_{D_2O})^{1/2}=$ 1.0264 at 100.0° and 1.0250 at 100.1°. The earlier data of Lewis and Macdonald [8] yield: $(p_{H_2O}/p_{D_2O})^{1/2}=1.026$ between 100.0° and 100.1°. Values of R obtained graphically from figure 3 are given in table 3. Although there appears to be a decreasing trend in the ratio with increase in D_2O, the precision of the graphical evaluation coupled with the small magnitude of the differences between boiling and condensation temperatures and the assumption that the differential ebulliometer is equivalent to exactly one theoretical plate does not justify recording R to better than 1 percent. The uncertainty in the value of R is relatively larger in the very dilute range. However, above 3% of D_2O the agreement of R with $(p_{H_2O}/p_{D_2O})^{1/2}$ is adequate to show that mixtures of D_2O and H_2O are nearly perfect solutions at the boiling point.

TABLE 3.—*Ratio of* D_2O/H_2O *in the liquid to* D_2O/H_2O *in the vapor*

Liquid		Vapor		R
Mole fraction	Mole ratio	Mole fraction	Mole ratio	
0.01	0.0101	0.0088	0.0089	1.13
.02	.0204	.0188	.0192	1.06
.03	.0309	.0287	.0296	1.04
.04	.0417	.0387	.0403	1.03
.05	.0526	.0485	.0510	1.03
.06	.0638	.0584	.0620	1.03
.07	.0753	.0684	.0734	1.03

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WASHINGTON, October 2, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP948

Part of Journal of Reasearch of the National Bureau of Standards, Volume 17, December 1936

ELECTRON CONCENTRATION AND SPECTRAL INTENSITY DISTRIBUTION IN A CESIUM DISCHARGE

By Fred L. Mohler

ABSTRACT

The theoretical relation between the transition probabilities for line emission in a given series and the probability of recombination into the final state of the series is derived from the postulate that the line intensity approaches the continuous intensity at the limit in thermal equilibrium. The measured values of A for the subordinate series of cesium lead to a value 1.7×10^{-21} cm² for the effective cross section for recombination of a 0.3-volt electron into the 6P limit. Measurements of recombination intensity and electron concentration have led to an identical value at low pressures, but the value apparently increased with pressure. It is concluded that probe measurements are systematically low at higher pressures and the intensity of the continuous spectrum is used as a basis for computing the true values of electron concentration N_e.

It has been shown that at pressures above 60 μ all the higher series lines have the same reversal temperature. One can define a temperature, T_s, by a given value of N_e in Saha's equation and the values so derived are equal to the reversal temperatures of the higher series lines. T_s is always less than the electron temperature but the two approach each other with increasing pressure.

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I. INTRODUCTION

A series [1] of papers has described a systematic study of the columnar discharge in cesium vapor in which various phenomena have been studied as a function of vapor pressure and current in a tube 1.8 cm in diameter. The data include electrical measurements of electron concentration and temperature, measurements of the number of excited atoms in different excited states, and measurements of intensity distribution in the line spectrum and in the continuous recombination spectrum. The purpose of finding general relations between the intensity distribution and the electrical conditions was not fully realized because of an apparent contradiction in the experimental data. In this paper the contradiction is removed by a more or less arbitrary

[1] F. L. Mohler, *Power input and dissipation in the positive column of a caesium discharge*, BS J. Research **9**, 25 (1932) RP455.
Collision of the first and second kind in the positive column of a caesium discharge, BS J. Research **9**, 493 (1932) RP485.
Recombination radiation in the cesium positive column, BS J. Research **10**, 771 (1933) RP565.
Reversal temperature and population of excited states in the cesium discharge, J. Research NBS **16**, 227 (1936) RP869.
Intensity distribution in the line emission spectrum of cesium, J. Research NBS **17**, 45 (1936) RP901.

choice between conflicting results, and a general relation is thereby derived which seems to justify the choice.

The dilemma arose in the measurements of the intensity of the continuous recombination spectrum as a function of the number of electrons per cubic centimeter, N_e. One would expect the intensity to depend only on the number of electrons and ions and on the electron velocity distribution. The experiments indicated that the intensity was from 10 to 40 times as great at a pressure of 300 microns of mercury as at 1 micron for equal values of N_e. This led to the assumption that the probability of recombination with emission of radiation depended on the vapor pressure.[2] The rate of recombination at higher pressures is known to depend on pressure, but the conventional view is that the process is radiationless. An alternative possibility is that the probe wire measurements of N_e are systematically in error at the higher pressures. Studies of the line intensity as a function of discharge conditions and consideration of the theoretical relation between line intensity and continuous intensity support the second alternative.[3]

II. RELATION BETWEEN THE PROBABILITY OF RECOMBINATION AND THE LINE TRANSITION PROBABILITIES

It is a familiar fact that an intense continuous spectrum beyond a series limit is always accompanied by relatively intense higher series lines which gradually merge into the continuum 50 or 100 A on the long wave length side of the theoretical limit and there is no perceptible discontinuity at the limit. The relation between line transition probabilities and the probability of recombination can conveniently be derived from the postulate that in thermal equilibrium the line intensity and the continuous intensity must similarly approach equality at the limit.

The intensity in ergs per cubic centimeter of radiation from a transition from the nth state of a series into a common final state is

$$J_n = N_n A_n h\nu, \tag{1}$$

where A_n is the transition probability and N_n is the population of the nth state. At a temperature, T,

$$N_n = N_1 \frac{g_n}{g_1} \exp.\ (-E_n/kT), \tag{2}$$

where E_n is the energy of the nth state relative to the normal state, N_1 is the population of the normal state, and g_n and g_1 are the weights of the two states. The average frequency interval between two successive lines of a hydrogen series, or any series if n is large, is

$$\delta\nu = 2R/n^3, \tag{3}$$

where R is the Rydberg frequency. In a finite interval, $\Delta\nu$, near the limit there are then $\Delta\nu n^3/2R$ lines and the integrated intensity is

$$\int_{\Delta\nu} \frac{J_n}{h\nu} d\nu = N_1 \frac{g_n}{g_1} \exp.\ (-E_n/kT) \int_{\Delta\nu} \frac{A_n n^3}{2R} d\nu,$$

[2] BS J. Research **10**, 771 (1933) RP565.
[3] J. Research NBS **17**, 45 (1936) RP901.

where E_n is an average value. Since $A_n n^3$ is a constant for large values of n

$$\int_{\Delta\nu} \frac{J_n}{h\nu} d\nu = N_1 \frac{g_n}{g_1} \exp.\ (-E_n/kT) \frac{A_n n^3}{2R} \Delta\nu. \tag{4}$$

The continuous spectrum arises from electrons with a continuous range of kinetic energy, E, falling into a level of limiting frequency, ν_i, with emission of radiation of frequency, ν, where

$$h\nu = h\nu_i + E. \tag{5}$$

The probability of capture into this level can be expressed in terms of the effective collision area, q. The number of effective collisions of electrons in an energy range, ΔE, with ions equals the number of quanta in the corresponding frequency range, $\Delta\nu$. In equilibrium the fraction of collisions in the energy range, ΔE, is given by kinetic theory, the number of ions and electrons is equal, and

$$\frac{J(\nu)\Delta\nu}{h\nu} = \frac{4\pi^{-1/2}h}{\sqrt{2m}} \frac{N_e^2}{(kT)^{3/2}} \exp.\ (-E/kT) Eq\Delta\nu. \tag{6}$$

Saha's equation gives for the value of N_e^2

$$N_e^2 = \frac{(2\pi m)^{3/2}}{h^3} (kT)^{3/2} \frac{2g^+}{g_1} N_1 \exp.\ (-E_i/kT), \tag{7}$$

where g^+ is the weight of the ionized state and E_i the ionization energy. Putting this value of N_e^2 in equation 6,

$$\frac{J(\nu)\Delta\nu}{h\nu} = \frac{16\pi m}{h^2} \frac{g^+}{g_1} N_1 \exp.\left(-\frac{E_i + E}{kT}\right) Eq\Delta\nu. \tag{8}$$

As E approaches zero, Eq remains finite [4] and the exponent approaches E_i/kT. In equation 4 the exponent has the same limiting value, and the condition that line and continuous spectra have equal intensities at the limit reduces to

$$Eq = \frac{h^2}{32\pi mR} \frac{g_n}{g^+} A_n n^3 = 1.45 \times 10^{-43} \frac{g_n}{g^+} A_n n^3. \tag{9}$$

This is not a new relation but could be derived from the law that the line absorption equals the continuous absorption at the limit.[5] The two products, Eq and An^3, are both roughly proportional to λ, and this approximation will be used in deriving values at the limit from observed values.

III. PROBABILITY OF RECOMBINATION INTO 6P OF CESIUM

Equation 9 will be used to compare experimental values of A_n for the subordinate series of cesium and q for the continuous spectrum beyond the 6P series limit. This is a doublet system with limits $\lambda_0 = 5080$ and 4944, the first being the more intense. For simplicity this will be treated as a single limit at $\lambda_0 = 5080$.

[4] Mohler and Boeckner, BS J. Research **2**, 489 (1929) RP46.
[5] Sugiura, J. Phys. **8**, 113 (1927).

Values [6] of A_n obtained in a limited range of discharge conditions (pressure greater than 60 μ) in which both N_n and J could be evaluated gave

$$A_n n^3 = 5.8 \times 10^8 \text{ at } \lambda 5080$$

for the sum of the doublet components. The integral on the left side of equation 4 must include all series with the common limit. For the S series, $g_n A_n$ is 0.1 times the value for the D series and for both

$$\frac{g_n}{g^+} A_n n^3 = 6.4 \times 10^9.$$

From equation 9, $Eq = 9.3 \times 10^{34}$ at $\lambda = 5080$. For comparison with the recombination spectrum, q will be evaluated at $E = 0.48 \times 10^{-12}$ erg or 0.3 electron volt, corresponding to 4520 A.

$$Eq = 8.3 \times 10^{-34}. \quad q = 1.72 \times 10^{-21} \text{ cm}^2.$$

The experimental value of q based on recombination measurements at low pressures is almost exactly this, viz., $q = 1.7 \times 10^{-21}$. The exact agreement is certainly accidental but the precision is sufficient to show that the values of A measured at high pressure are consistent with the low-pressure values of q and not with the high-pressure values which are over 10 times as great. The value 1.7×10^{-21} cm^2 is of the same magnitude as the theoretical value for recombination of a 0.3-volt electron into the 2_2 level of hydrogen, viz., 3.66×10^{-21} cm^2.[7]

These considerations strongly support the conclusion that there is a systematic error in the probe measurements of N_e used in computing values of q from the observed intensity of the recombination spectrum. A possible explanation of the error is that the current to the probe lowers the concentration of the electrons in the plasma near the probe. Such an effect would increase with pressure and the magnitude of the effect seems sufficient to account for the discrepancy. The theory of probe measurements is rigorous only at low pressures and the best experimental checks on the theory have been made at low pressures.[8] There are many possible complications at higher pressures [9] and no assurance that the electron diffusion effect is predominant.

IV. ELECTRON CONCENTRATION FROM INTENSITY MEASUREMENTS

There is no reason to doubt the constancy of atomic transition probabilities, and the intensity of the recombination spectrum can be used to compute values of N_e. The author has published intensity measurements as a function of apparent values of N_e for pressures ranging from 0.78 to 290 μ.[10] There is roughly a twofold change in electron temperature in this range and equation 6 shows that the intensity at the limit varies inversely as $T^{3/2}$. Figure 1 gives a

[6] J. Research NBS **17**, 45 (1936) RP901.
[7] Stueckelberg and Morse, Phys. Rev. **36**, 16, (1930).
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[10] BS J. Research **10**, 771 (1933) RP565.

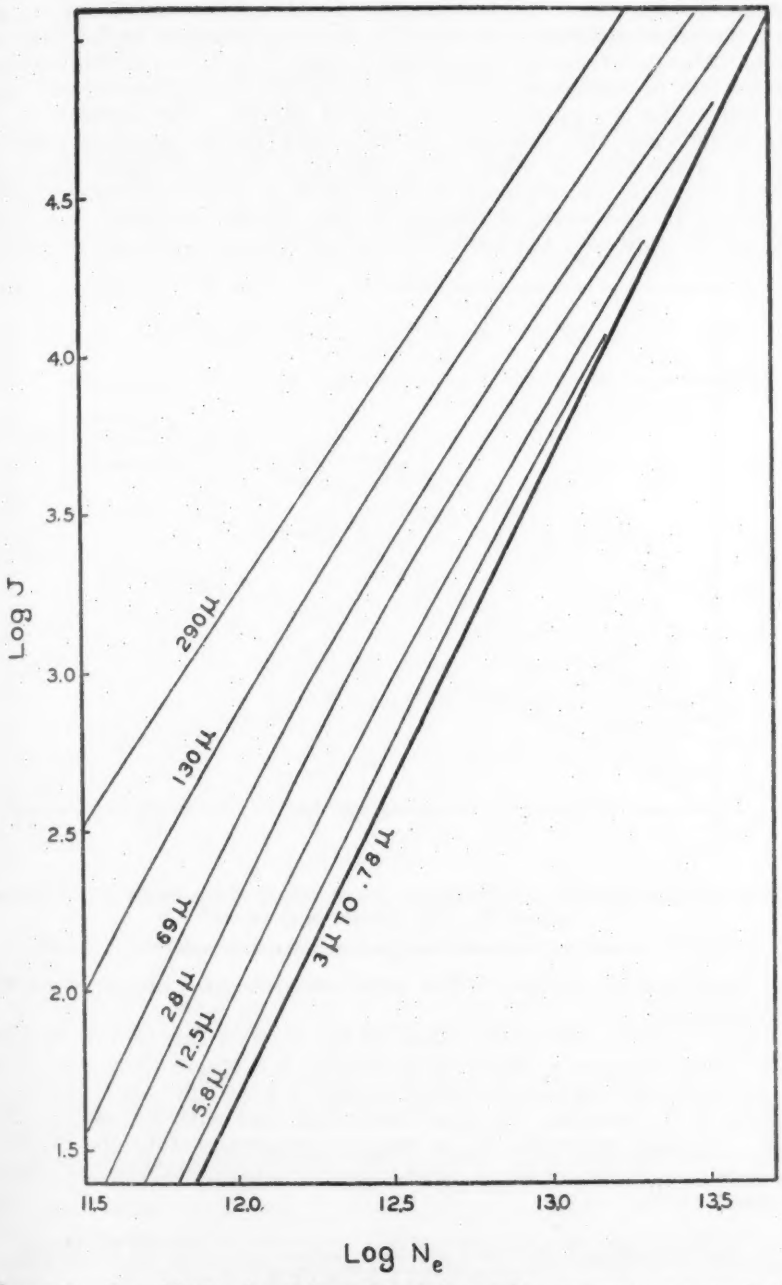

FIGURE 1.—*Logarithmic plot of intensity of the continuous spectrum near the* 6P *limit versus the observed electron concentration.*

Observed values of J are reduced to a standard electron temperature of 3,480° K

logarithmic plot of intensity versus measured values of N_e. Observed intensities have been multiplied by $(T_e/3480)^{3/2}$ to reduce all values to a standard temperature of 3,480° K corresponding to 0.3 electron volt. Measurements in the pressure range 3 to 0.78 μ give intensities accurately proportional to N^2_e and independent of pressure and lead to the value $q=1.7\times10^{-21}$ cm^2 quoted above. The horizontal interval between the observed curve at any higher pressure and the curve on the right is taken to be the log of the correction factor by which apparent values must be multiplied to give true values. Fortunately, in the series of papers on the cesium discharge numerical values involving N_e are based largely on low-pressure measurements

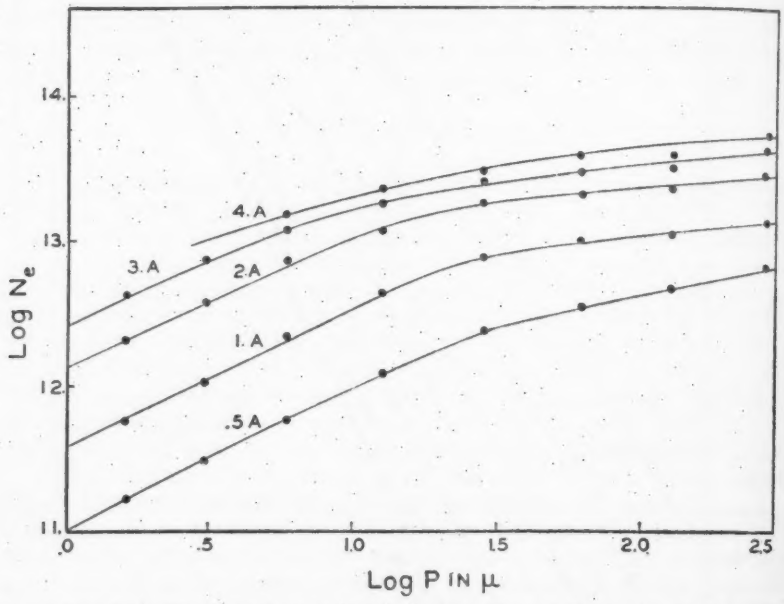

FIGURE 2.—*Logarithmic plot of electron concentration at the center of the positive column in a tube 1.8* cm *in diameter.*

Values of N_e are based on low-pressure probe measurements and the recombination intensity.

and need not be revised. The only exception is the paper on recombination.

Figure 2 gives corrected values of log N_e as a function of log p in microns for various currents in a column 1.8 cm in diameter. The values are based on the maximum intensity near the axis of the tube. Values of N_e increase, but at a decreasing rate with increasing pressure. At high pressures N_e is roughly proportional to the current, while at low pressures the change is nearly proportional to the square of the current.

V. EQUILIBRIUM BETWEEN EXCITED STATES AND IONIZED STATES

Direct measurements of the reversal temperature of the higher series lines of the principal series [11] and intensity measurements in S, D, and F series indicate that at pressures of the order of 100 μ all

[11] J. Research NBS **16**, 227 (1936) RP869; **17**, 45 (1936) RP901.

states beyond the third in each series have the same reversal temperature. The number of atoms in a given state, N_n, is related to the reversal temperature, T_n, by an equation of the Boltzman form.

$$N_n = N_1 \frac{g_n}{g_1} \exp.\ (-E_n/kT_n). \tag{10}$$

There is then a temperature distribution of excitation among the higher states and the theoretical considerations of the first section suggest that this common value of T_n must be related to the electron concentration, N_e. By equation 10 a value of T_n is defined by a given value, N_n, without any assumption as to equilibrium, and in the same way one can define a temperature, T_s, by the use of Saha's equation and a given value of N_e,

$$N_e^2 = 2.43 \times 10^{15} \frac{g^+}{g_1} N_1 T_s^{3/2} \exp.\ (-E_i/kT_s) \tag{11}$$

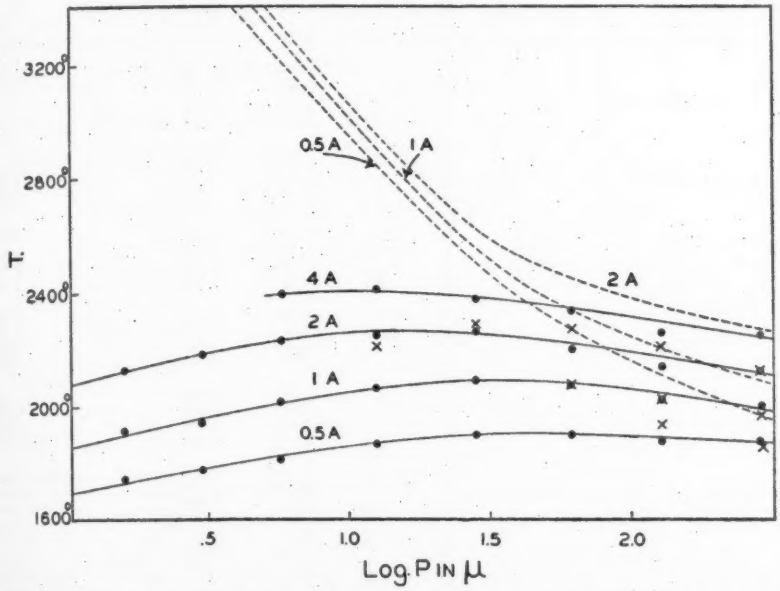

FIGURE 3.—*Full lines and dots give T_s based on values of N_e from figure 2 and Saha's equation; crosses give reversal temperatures of higher series lines and broken lines give the reversal temperatures of the resonance doublet which is nearly equal to T_e.*

It can be seen from the derivation of equation 9 that if the line intensity approaches the continuous intensity at the limit then T_n must approach T_s.

Values of N_e from figure 2 have been used to compute values of T_s, and table 1 and figure 3 show that there is a fairly satisfactory agreement between T_n and T_s in the range in which T_n can be evaluated. This consistency of the results justifies the method of basing values of N_e on intensity measurements, for the correction brings a wide range of experimental data into fair agreement.

The common value of T_n and T_s is much less than the electron temperature, while the reversal temperature of the first doublet of the principal series, T (2P), is nearly equal to the electron temperature

except at very low pressures.[12] Values of T (2P) have been included in figure 3 and table 1. The two temperatures, T_e and T_s, define the electrical conditions in the plasma. The one gives the velocity distribution of the electrons and the other the number of electrons and ions per cubic centimeter for a given value of N_a. At high pressures where electrical methods fail, both can be measured by optical methods. The intensity of the continuum near a series limit gives T_s, and the intensity distribution depends on T_e.[13]

TABLE 1.—*Electron concentration, T_s, and reversal temperatures for a positive column in cesium vapor*

P	Current	Log N_e corrected	T_s	T_s higher lines	T (6P)
μ	amp		°K		
290	4	13.73	2,250	----------	----------
	2	13.46	2,125	2,115	2,260
	1	13.14	2,000	1,970	2,090
	.5	12.82	1,880	1,860	1,950
130	4	13.59	2,260	----------	----------
	2	13.35	2,140	2,205	2,400
	1	13.04	2,020	2,030	2,230
	.5	12.66	1,875	1,938	2,140
69	4	13.58	2,335	----------	----------
	2	13.32	2,200	2,270	2,450
	1	13.00	2,070	2,080	2,340
	.5	12.55	1,900	2,045	2,260
28	4	13.46	2,375	----------	2,740
	2	13.26	2,260	(2,290)	2,600
	1	12.88	2,090	----------	2,530
	.5	12.38	1,900	----------	2,500
12.5	4	13.36	2,410	----------	3,050
	2	13.05	2,245	(2,210)	2,920
	1	12.64	2,060	----------	2,890
	.5	12.10	1,860	----------	2,860
5.8	4	13.15	2,385	----------	----------
	2	12.85	2,230	----------	3,280
	1	12.33	2,010	----------	3,280
	.5	11.76	1,810	----------	3,200
3	2	12.57	2,180	----------	----------
	1	12.02	1,940	----------	----------
	.5	11.48	1,775	----------	----------
1.6	2	12.31	2,125	----------	----------
	1	11.76	1,910	----------	----------
	.5	11.22	1,740	----------	----------

The elementary interactions between electrons, atoms, and radiation in a discharge become very complicated with increasing pressure, but these processes gradually approach equilibrium with each other so that statistically the discharge conditions become simpler as pressure and current increase. At extremely low pressures the plasma electrons take up a temperature distribution of velocity. (The mechanism is not entirely clear.) Above a pressure of 10 μ collisions of the first and second kind keep the number of atoms in the first excited state nearly in equilibrium with the electron temperature. Ionization of highly excited states and recombination into these states bring the number of ions and of excited states to equilibrium near 60 μ. Above this pressure the intensity of the higher series lines and of the continuum near the limit is characteristic of the temperature, T_s, but the population of the first excited state and the intensity distri-

[12] BS J. Research 9, 493 (1932) RP485.
[13] Mohler and Boeckner, BS J. Research 3, 303 (1929) RP96.

bution in the continuum depend on T_e. It is seen from figure 3 that these two temperatures approach each other with increasing pressure. Presumably recombination on the tube walls keeps T_e below T_e, and they will approach equality when spacere combination becomes predominant. Then one temperature will define electrical conditions and spectral intensity distribution for a given value of N_a. The gas temperature has been assumed to be the wall temperature, but is probably appreciably above this at the higher pressures, and the value of N_a becomes uncertain.

Studies of arcs at atmospheric pressure [14] indicate that the gas temperature in the core of the discharge is nearly equal to the electron temperature. This last stage in the approach to equilibrium is probably not approached in the range of pressure studied here.

I am indebted to Dr. C. Boeckner for pointing out the possibility that probe measurements of electron concentration may be systematically low at higher pressures.

WASHINGTON, October 16, 1936.

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP949

Part of Journal of Research of the National Bureau of Standards, Volume 17, December 1936

STUDY OF THE EFFECT OF FIBER COMPONENTS ON THE STABILITY OF BOOK PAPERS

By Merle B. Shaw and Martin J. O'Leary

ABSTRACT

Supplementing previously reported studies relating to the permanence of writing papers used for records, an investigation of the relation of papermaking materials and processes to the stability and other properties of book papers is in progress. This article reports the results of tests of a number of pulps commonly used in fine printing papers as regards the stability of experimental unsized papers made from them. The effect of filling and sizing materials, respectively, will be reported in subsequent papers.

The papermaking fibers used were representative commercial materials and consisted of four kinds of purified wood pulp, soda pulp and sulphite pulp (mixed in beater furnish), new rags (no. 1 white shirt cuttings), and old rags (no. 1 old whites and twos and blues, blended in the beater.) The pulps and half-stuffs ranged in quality from 78 to 93 percent of alpha-cellulose and from 3.8 to 0.4 in copper number. The composition of the beater furnishes was 85 percent of fiber and 15 percent of clay, which is a proportion commonly used for book papers.

The experimental papers made from the rags had the characteristics of good book papers and showed no appreciable change in the accelerated aging (heat) test, which indicates a very high degree of permanence. One of the purified wood pulps produced a relatively stable sheet of satisfactory book-paper quality. The papers made from two of the wood pulps were somewhat less stable in the accelerated aging test, but that made from the remaining purified wood pulp was strong and relatively stable. The paper produced from the mixture of sulphite pulp and soda pulp was considerably less stable than the papers made from the purer fibers. A close relation was shown between the cellulosic purity of the fibers and the stability of the unsized papers made from them, but only a small amount of alum and no rosin size were used in the manufacturing process. The effect of these variables on the stability of the papers will be studied in the second part of the investigation.

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I. INTRODUCTION

As a part of its program of research relating to the stability of papers used for records, the National Bureau of Standards is making a study of the relation of papermaking materials and processes to the strength, stability, and other properties of book papers. This study is the fourth

in a series planned to include all the important types of fibrous raw materials commonly used in the manufacture of record papers. The three preceding studies related to writing papers [1, 2, 3].[1]

A suggested classification and specification of book papers for record purposes published by the Bureau [4] comprise four classes, ranging from papers for permanent records to those suitable for temporary use only. The classification and specification were based on tests of commercial papers. The results of the tests showed that the stability of book papers, as was found also for writing papers, is not always commensurate with the quality of the fibers used in their manufacture. It is believed that papermaking studies made under the carefully controlled conditions possible with the semicommercial equipment of the Bureau should indicate the best practice for obtaining the optimum results with each kind of fiber and other raw materials. The commercial application of such knowledge should ultimately lead to improved quality of papers with respect to their endurance.

The study of book papers will necessarily be much more extensive than that of the writing papers [1, 2, 3] because of the greater variety of materials used in book papers. This is true not only with respect to the fiber components but also to the use of filling and coating materials. Because of the considerable time required to complete the program as a whole, it has been divided into three subprojects. The first is a study of the fibers commonly used. The other two will deal with the effect of filling and sizing materials and the effect of mineral coating materials, respectively, on the stability and strength of book papers. The present article is a report of the relation of chemical characteristics of fibers of different degrees of purity to the stability of papers made from them. The alpha-cellulose content and the copper number have been found to be closely related to the stability of paper—high alpha-cellulose content and low copper number being characteristics of stable paper. In this work consideration has been given also to beta- and gamma-celluloses and to pentosans.

II. FIBERS USED

It should be kept in mind that this is not a general study of the manufacture of book papers, but is a study made primarily to obtain information to assist in the specification of book papers for printed records. Since the papers to be made will therefore be limited to a sufficient number for this purpose only, the selection of fibrous materials to be employed in the investigation covered the range of those commonly used in the fine printing papers.

The fibers were obtained from commercial manufacturers. They consisted of four wood pulps produced with special pulping and bleaching treatments to obtain high purity and strength; soda pulp and sulphite pulp of the ordinary book-paper grade; new rags, the grade known commercially as no. 1 white shirt cuttings; and two grades of old rags, no. 1 old whites and "twos and blues."

III. PAPERMAKING EQUIPMENT

The Bureau paper mill contains equipment for the experimental manufacture of practically all types of paper under conditions which in general simulate those of industrial mills. Figures 1 and 2 show

[1] Numbers in brackets refer to the list of references at the end of this paper.

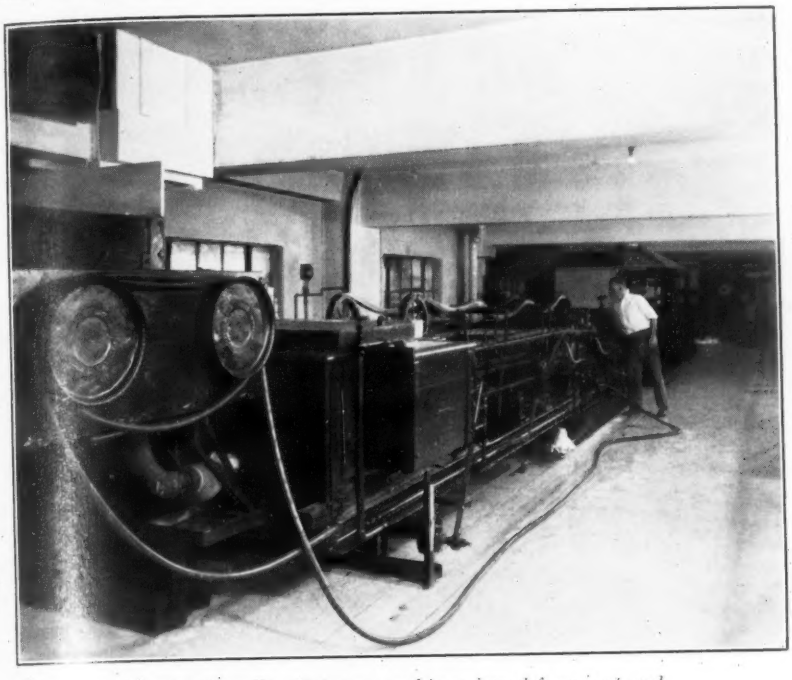

FIGURE 1.—*Fourdrinier machine viewed from wet end.*

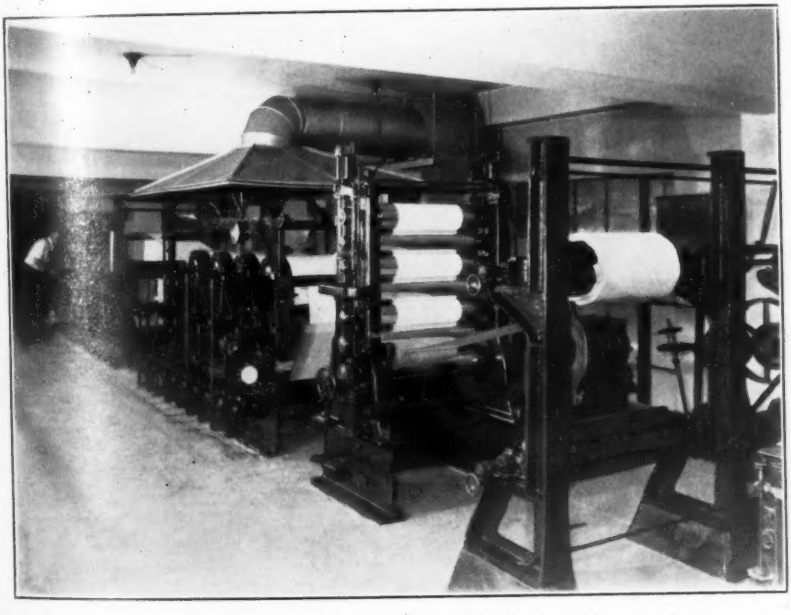

FIGURE 2.—*Fourdrinier machine viewed from dry end.*

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the experimental paper machine. A complete description and other photographs of the equipment may be found in previous publications [5].

IV. PAPERMAKING PROCESSES

The methods of beating and paper-machine operation followed very closely those described in the other publications of this investigation [1, 2, 3]. The reader is referred to them for details.

V. TEST METHODS

The physical and most of the chemical tests of the fibrous materials and of the papers were made in accordance with the official methods [2] of the Technical Association of the Pulp and Paper Industry. An improved volumetric method developed at the Bureau by H. F. Launer was used to determine the alpha-, beta-, and gamma-celluloses. In this method the fibers are treated with an approximately $2M$ solution of sodium hydroxide. The entire alpha-cellulose residue, as well as portions of the filtrate, is quantitatively oxidized by dichromate, and the proportions of the constituents in the sample are calculated on the basis of the dichromate data alone.[3] The method used for determining the pentosans (complex carbohydrates widely distributed in plants which yield pentoses on hydrolysis) was essentially the same as the method that has previously been regularly used. The pH was determined electrometrically, using a quinhydrone and also a glass electrode.

The relative stability of papers cannot be determined by analysis of the original papers alone. Therefore, the pertinent physical and chemical tests were applied not only to the original papers but to samples that had been submitted to an accelerated aging test as well. This test is made at the Bureau by heating specimens of the paper for 72 hours at 100° C and then determining to what extent the paper has been altered in folding endurance, tearing strength, alpha-cellulose content, and copper number. For details of this test the reader is referred to previous discussions of the method [6].

VI. ANALYSES OF PAPERMAKING MATERIALS USED

1. FIBERS

Analyses showing the degree of cellulosic purity of the wood pulps and the various grades of rag half-stuffs (partially pulped rags that have been boiled, washed, and drawn out of weave) used in the manufacture of the papers are given in table 1. The pulps and half-stuffs ranged in quality from 78 to 93 percent of alpha-cellulose and from 3.8 to 0.4 in copper number. The method employed in preparing the rag half-stuffs was the same as that described in detail in an earlier publication [3].

[2] Copies of the methods can be obtained from the Technical Association of the Pulp and Paper Industry, 122 East 42d Street, New York, N. Y.

[3] The method will be described in detail later in a Bureau publication on the subject.

TABLE 1.—*Chemical test data on fibrous materials used*

Fibrous material	Alpha-cellulose	Beta-cellulose	Gamma cellulose	Pentosans	Copper number	Ash	Resin
	%[2]	%[2]	%[2]	%		%	%
Purified wood pulp *A*[1]	90.6	4.8	4.6	3.8	0.72	0.11	0.24
Purified wood pulp *B*[1]	87.8	6.7	5.5	6.0	.86	.19	.26
Purified wood pulp *C*[1]	88.0	6.2	5.8	5.6	.69	.10	.13
Purified wood pulp *D*[1]	84.1	4.7	11.2	10.3	.72	.16	.13
Sulphite pulp	82.0	5.4	12.6	6.2	3.34	.26	.70
Soda pulp	78.2	18.6	3.2	21.3	3.83	.42	.20
No. 1 new white rags, bleached half-stuff	93.0	6.4	.6	.8	.38	.12	.....
No. 1 old white rags, bleached half-stuff	90.3	8.9	.8	.5	.41	.16	.....
Twos and blues, bleached half-stuff	90.5	8.4	1.1	.5	.49	.22	.....

[1] These pulps were produced by special cooking and bleaching treatments to obtain improved quality.
[2] Based on total cellulose.

2. CLAY

The clay used was a domestic commercial filler clay. The following analysis [4] shows its composition.

Loss at 105° C	0.3%.
Further loss on ignition	13.7%.
Silica (SiO_2)	45.3%.
Iron oxide (Fe_2O_3)	0.2%.
Alumina (Al_2O_3)	38.8%.
Titanium oxide (TiO_2)	1.8%.
Calcium oxide (CaO)	Not detected.
Magnesium oxide (MgO)	Not detected.

VII. DATA ON PAPERS MADE

The composition of the beater furnishes (materials blended in the beater), regardless of the kind of fibrous material, was 85 percent of fiber and 15 percent of clay, a proportion common for book papers. No rosin was added. Just enough alum (aluminum sulphate) was used to clear the water in the beater in the first few runs. After the amount required had been established the quantity was kept practically constant for the remaining runs irrespective of the appearance of the water.

Data relative to the beater furnish and the beating time for each paper-machine run and various measurements on the papers made are given in tables 2, 3, and 4.

[4] Made by Chemistry Division, National Bureau of Standards.

TABLE 2.—*Papermaking details and some physical properties of the book papers*

Paper machine run number	Beater furnish				Tests of papers [4]							
	Fiber [1]	Alum (based on dry furnish)	Beating interval	Acidity of stock at head box (quinhydrone method)	Weight: 25 by 40 inches, 500 sheets	Bursting strength	Tensile properties: Breaking load [3]		Tensile properties: Elongation at rupture		Thickness	Opacity
							Machine direction	Cross direction	Machine direction	Cross direction		
		%	hr	pH	lb	*Points* [2]	kg	kg	%	%	in.	%
1102	Purified wood pulp *A*	0.4	5	6.7±	56.3	21	3.8	2.5	1.2	4.4	0.0036	90
1103	do	.4	5	6.7±	56.0	22	4.4	2.9	2.0	5.9	.0035	90
1104	Purified wood pulp *B*	.4	5	6.7±	54.2	33	6.8	4.0	2.7	6.3	.0034	88
1106	do	.5	6	6.8±	56.3	40	8.8	4.5	2.6	7.9	.0033	89
1105	75% of pulp *A*, 25% of pulp *B*	.4	5½	6.6±	56.5	24	5.3	3.1	2.1	5.9	.0037	89
1110	Purified wood pulp *C*	.5	5½	6.5±	57.5	33	7.1	4.4	2.5	8.0	.0036	87
1107	Purified wood pulp *D*	.5	5½	6.9±	53.9	34	8.4	5.7	2.3	7.6	.0033	82
1108	do	.5	6	6.2±	55.4	37	8.0	5.9	2.5	8.2	.0034	82
1111	50% of sulphite, 50% of soda pulp.	.5	5	6.7±	56.1	22	5.9	3.8	1.9	5.5	.0040	87
1112	do	.5	4	6.7±	54.9	22	5.5	3.4	1.5	3.5	.0039	87
1113	No. 1 new white rags (half-stuff).	.5	5	6.8±	56.0	17	4.6	3.1	2.5	5.0	.0036	90
1114	do	.5	5	6.9±	54.1	18	4.8	3.0	2.0	4.5	.0035	90
1115	Old rags [5] (half-stuff)	.5	5½	6.7±	55.8	15	3.7	2.4	2.0	4.0	.0040	92
1116	do	.5	4	6.5±	55.9	13	3.1	2.2	2.0	3.0	.0040	93

[1] Beater furnish for each run was 85 percent of fiber and 15 percent of clay.
[2] Bursting pressure, in pounds per square inch, through a circular orifice 1.2 inches in diameter.
[3] For test specimen 15 mm wide and 100 mm between jaws.
[4] All physical tests made at 65 percent relative humidity and 70° F.
[5] 50% of no. 1 old whites, 50% of twos and blues.

TABLE 3.—*Folding endurance and tearing strength data on the book papers*

Paper machine run number	Fiber composition	Tests of unheated papers [2]						Tests of heat-treated papers [3]		
		Folding endurance [1]				Tearing strength				
		Schopper		MIT						
		Machine direction	Cross direction	Machine direction	Cross direction	Machine direction	Cross direction	Folding endurance in percentage of initial strength, Schopper	Folding endurance in percentage of initial strength, MIT	Tearing strength in percentage of initial strength
		Double folds	*Double folds*	*Double folds*	*Double folds*	g	g			
1102	Purified wood pulp *A*	78	34	[4] 1,675	[4] 485	70	72	95	89	100
1103	do	74	32	[4] 1,715	[4] 400	66	70	100	85	103
1104	Purified wood pulp *B*	2,200	730	[5] 1,230	[5] 190	128	136	69	78	88
1106	do	3,300	2,000	[5] 1,750	[5] 660	104	128	80	79	96
1105	75% of pulp *A*, 25% of pulp *B*.	180	70	[4] 3,000	[4] 1,540	84	92	101	111	96
1110	Purified wood pulp *C*	1,760	1,140	[5] 890	[5] 260	109	96	83	78	96
1107	Purified wood pulp *D*	2,400	2,190	[5] 1,510	[5] 830	95	110	87	98	104
1108	do	1,830	3,820	[5] 1,520	[5] 2,020	93	102	83	80	102
1111	50% of sulphite, 50% of soda pulp.	85	44	[4] 1,120	[4] 395	54	60	57	68	96
1112	do	66	34	[4] 1,120	[4] 285	53	59	55	53	94
1113	No. 1 new white rags (half-stuff).	63	51	[4] 1,250	[4] 765	98	88	130	103	97
1114	do	143	65	[4] 2,866	[4] 1,078	95	91	105	90	104
1115	Old rags (half-stuff)	21	10	[4] 120	[4] 70	63	71	95	123	98
1116	do	11	8	[4] 80	[4] 50	66	66	109	98	98

[1] Test specimen 15 mm wide.
[2] All physical tests made at 65-percent relative humidity and 70° F.
[3] San ples heated at 100° C for 72 hours.
[4] Tests made at 0.5-kg tension.
[5] Tests made at 1-kg tension.

TABLE 4.—*Chemical data on the book papers*

Paper machine run number	Fiber composition	Original papers								Heat-treated papers[2]				
				Acidity						Change in content				
		Ash	Resin	Extract, Kohler-Hall method	pH of extract (glass-electrode method)	Alpha-cellulose, based on total cellulose	Beta-cellulose, based on total cellulose	Gamma-cellulose, based on total cellulose	Pentosans	Copper number	Alpha-cellulose	Beta-cellulose	Gamma-cellulose	Pentosans	Copper number
		%	%	%[1]		%	%	%	%		%	%	%	%	
1102	Purified wood pulp *A*	10.8	0.22	0.006	6.5±	90.2	3.2	6.6	3.9	0.70	−0.2	+0.2	0.0	0.0	+0.15
1103	do	11.5	.22	.006	6.5±	90.9	2.7	6.4	4.2	.71	−.7	+2.4	−1.7	−.2	.13
1104	Purified wood pulp *B*	10.7	.24	.011	6.4±	85.7	6.7	7.6	6.3	.88	−.2	+.2	.0	−.1	.29
1106	do	11.4	.26	.010	6.8±	85.2	6.2	8.6	5.6	.90	−1.0	+2.0	−1.0	.0	.17
1105	75% of pulp A, 25% of pulp *B*	11.0	.20	.001	7.3±	89.6	4.6	5.8	3.7	.77	−.4	+.4	.0	+.1	.17
1110	Purified wood pulp *C*	11.9	.13	.010	6.6±	85.1	8.7	6.2	5.6	.81	.0	+.3	−.3	−.1	.15
1107	Purified wood pulp *D*	12.2	.13	.010	6.7±	82.6	2.4	15.0	10.6	.85	−.4	+.2	+.2	+.1	.10
1108	do	12.4	.13	.008	6.7±	82.4	3.0	14.6	10.7	.87	−1.0	+.5	+.5	+.1	.10
1111	50% of sulphite, 50% of soda pulp	5.3	.40	.017	6.2±	77.8	14.5	7.7	13.9	2.75	−.4	−1.0	+1.4	+.1	.31
1112	do	5.7	.50	.021	6.1±	77.7	15.1	7.2	14.2	3.02	−1.0	+1.2	+.2	−.7	.27
1113	No. 1 new white rags (half-stuff)	11.6	.24	.004	7.0±	95.2	4.2	.6	.6	.33	+.2	−.6	+.4	.0	.03
1114	do	11.6	.22	.010	6.8±	95.0	4.2	.8	.8	.35	−.2	+.2	.0	−.1	.04
1115	Old rags (half-stuff)	12.7	.29	.001	7.3±	92.6	6.7	.7	.7	.43	−.6	+.3	+.3	.0	.05
1116	do	12.5	.36	.002	7.3±	92.8	6.5	.7	.8	.39	−1.0	+.9	+.1	−.1	.10

[1] Acidity expressed as percent of SO_3.
[2] Samples heated at 100° C for 72 hours.

Purified wood pulp A.—The procedure followed in the beating treatment of purified wood pulp *A*, runs nos. 1102 and 1103, was that considered suitable for producing a good book paper. The beaten fibers were long but remained separate and did not ball or clot during the beating, and screened, through 0.014-inch slots, exceptionally well for such long fibers. The beating time was 5 hours.

Because of difficulties in adjusting the paper machine and the weight of the paper during run no. 1102, the run was repeated (no. 1103). The finished papers of the two runs were considered very satisfactory. The data given in tables 3 and 4 indicate that they were also relatively stable, being little changed in alpha-cellulose content, copper number, folding endurance, and tearing strength after oven aging.

Purified wood pulp B.—The beating treatment given the pulp for run no. 1104 was similar to that given purified wood pulp *A*, runs nos. 1102 and 1103, but the beaten fibers seemed "brash" (were not soft and pliable) and the formation of the sheet was not good.

For machine run no. 1106 the beater was furnished lighter, that is, with lower stock consistency, to promote faster circulation of the stock, and the beater roll was lowered more rapidly to the plate to cut up the fibers more quickly. The pulp was beaten hard for 6 hours, yet the fibers remained long. The stock caused no trouble on the paper machine, and handled much better than that for run no. 1104. The results were better with the thinner consistency, but the paper seemed too hard and was not so well closed a sheet as is desirable for book paper.

It is apparent that the beater roll of the Bureau's 50-pound beater is not heavy enough, nor the beating tackle (bars of beater roll and bed plate) thin and sharp enough, to cut strong long-fibered pulp as quickly as is required to produce soft, bulky printing paper. The longer beating time required with the relatively light roll equipped with comparatively blunt tackle results in a sheet that is less opaque and harder than is suitable for book papers, but it would be satisfactory for writing papers.

The color of purified wood pulp *B* was not so good as that of pulp *A*. The test data on the cellulosic purity of the papers and their stability toward the heat test show the life expectancy of that made from pulp *B* to be less also.

After run no. 1104 was made it was learned that pulp *B* is not intended to be used as an entire fiber furnish for book paper, but is recommended as a part-furnish to increase the strength of the weaker pulp. The following run was made from such a mixed furnish.

Purified wood pulps A and B (mixed furnish).—The fibrous material of the beater furnish for run no. 1105 was 75 percent of purified wood pulp *A* and 25 percent of purified wood pulp *B*. The run was made to determine whether the addition of pulp *B* would strengthen the sheet without impairing its stability. The test data indicate that the addition of the small amount of the relatively strong pulp to the weaker pulp of greater stability gave a stronger sheet than the weaker pulp alone, without appreciably lessening the stability of the paper.

Purified wood pulp C.—Pulp *C* is recommended by the manufacturer for use if paper of fair strength for book purposes is wanted. Pulp *C*, run no. 1110, was more susceptible to hydration than pulp *A*, and the finished paper was harder than that made from pulp *A* (runs nos. 1102 and 1103), but softer than that made from pulp *B* (runs nos. 1104 and 1106). The color was better than that of pulp *B*. The test data show the paper to be strong and fairly stable.

Purified wood pulp D.—The beating treatment given the pulp for run no. 1107 was the same as that given the mixture of purified wood pulps *A* and *B*, run no. 1105. The fibers were long and clotted together even after the completion of the beating and were difficult to separate in the subsequent operations. For machine run no. 1108 the beater was furnished lighter to facilitate faster circulation and the beater roll was lowered rapidly to the plate to cut the fibers and produce free-beaten stock. The pulp was beaten for 6 hours, but the fibers still remained long. The finished papers of both runs were hard.

Again it is apparent that the beater roll and beating tackle are not suited to the requirements of hard long-fibered pulp to get the character of sheet for book papers. Different types of paper require different treatment in the beater. The making of book papers, in common with other papers requiring bulk and absorptive qualities, depends chiefly on quick beating with sharp tackle, the beater being furnished light and the beating being effected quickly enough to prevent excessive hydration yet producing the desired fraying and fibrillation of the individual fibers.

The test data show that pulp *D* and the papers made from it were strong and relatively stable. If the beating of the pulp could be carried out quickly to preclude excessive hydrating, or gelatinizing, effect on the fibers, a soft bulky sheet suitable for book paper would doubtless be produced and would have the necessary strength for severe service.

Sulphite and soda pulp mixture.—The pulp for the beater furnishes for runs nos. 1111 and 1112 was sulphite and soda, mixed in equal quantities. The beating treatment for run no. 1111 was merely a light brushing of the pulp. The water in the beater did not clear when the alum was added, and the machine water at the head box was not clear, but since the present subproject is limited to the pulps, no more alum was added. The stock was very free (drained quickly) on the paper-machine wire.

For machine run no. 1112 the percentages of pulps and clay were the same as for run no. 1111, but the beating was more drastic and of shorter duration. The behavior of the clay in the beater water and the machine water was the same as that reported for run no. 1111.

As indicated by the percentage of ash, table 4, the retention of clay in the papers was comparatively low. With regard to retention of filler, Steele [7] states that "Pigments can be retained in paper by any of three mechanisms, namely, filtration, coflocculation, and mechanical attachment." The appearance of the beater and machine waters of runs nos. 1111 and 1112 indicates that the flocculation was very low. Since the beater water for the other pulps was relatively clear, and since the same amount of alum was added and the same clay was used for all the runs, the retention of clay in the other papers must have been due mainly to mechanical attachment. The effect of larger amounts of alum, and of the use of rosin size, on the retention of clay in the sulphite-soda pulp mixture will be studied in the second part of the investigation of book papers.

The test data show that the papers were not of very high stability as regards retention of folding endurance, although the changes in alpha-cellulose content and in copper number were not large.

New rags.—The rag fiber of the beater furnish for runs nos. 1113 and 1114 was half-stuff made from no. 1 white shirt cuttings. As the severity of beating required for the new rags for book papers had not been determined, the furnish for run no. 1113 was given a fairly hard beating treatment. For run no. 1114 the beating interval was the same as for run no. 1113, but the operation was less drastic, leaving the fibers longer.

The papers made from the new white rags were very satisfactory as to character of sheet and judging from the test data were of a high degree of stability.

Old rags.—The beater furnish for run no. 1115 consisted of equal parts of half-stuffs made from no. 1 old whites and from twos and blues. The stock was prepared by a very mild beating action. Run no. 1116 was similar to run no. 1115 except that the beating treatment was of shorter duration and was more severe. The papers made were soft and of good formation. They were excellent book papers in appearance, and the test data indicate that they were also of good stability.

VIII. SUMMARY AND DISCUSSION

The data show that a number of the pulps commonly used in the manufacture of book papers are suitable for papers that must meet specifications requiring a high degree of permanence.

The experimental papers made from the rags (no. 1 white shirt cuttings or the mixture of no. 1 old whites and twos and blues) were excellent in appearance and possessed the softness, bulk, and opacity which are requisite characteristics of book papers. The fact that the folding endurance suffered no appreciable loss in the heat treatment indicates that very stable paper can be made from this type of fiber.

Purified wood pulp *A* produced a relatively stable sheet of satisfactory book-paper quality, although weaker than that made from purified wood pulps *B* or *C*. The folding endurance and tearing strength of book papers, however, are not such important factors as in the case of writing papers, which are subjected to greater stresses, but they are significant in interpreting the results of the aging treatment.

The paper made from purified wood pulp *B* or *C* used as an entire fiber furnish was stronger but harder and less stable to the heat test than that made from pulp *A*. The paper produced from purified wood pulp *D* also was hard but it was strong and of relatively stable quality. It is believed that the hardness of the papers made from these pulps was due to the beater not being suited to the requirements of strong long-fibered pulp to produce soft, opaque printing paper. Papers requiring bulk and absorptive qualities depend chiefly on quick beating with sharp tackle to prevent excessive hydration yet produce the desired fraying and fibrillation of the individual fibers. The longer beating time required with the relatively light roll and blunt tackle of the beater used at the Bureau resulted in a harder and less opaque sheet. If the beating were carried out quickly enough to preclude excessive hydration of the fibers a soft, bulky sheet of sufficient strength for severe service would doubtless be produced.

The paper produced from the mixture of sulphite pulp and soda pulp was considerably less stable than that made from the purer fibers. During the manufacturing process the water was not clear in

the beater nor at the head box, and the retention of clay in the paper was comparatively low, but since the next phase of the study of book papers includes detailed investigation of the effects of larger amounts of alum and the use of rosin size, no further consideration was given at this time to the behavior of the clay as regards retention.

Since clay is chemically inert, and not enough alum was used to adversely affect the papers, any deterioration occurring under the heat test must be ascribed to the cellulosic components. Resin is present only in such small amounts that it can be disregarded.

The changes in the beta- and the gamma-cellulose contents of the heat-treated papers were not significant enough to warrant the use of these values as criteria of the stability of the papers. The present belief that alpha-cellulose content and copper number are closely related to stability of paper, and that high alpha-cellulose content and low copper number, with very little change in these attributes when the papers are heated, are characteristics of stable paper, is supported by the data.

The pentosan content of the different papers was not appreciably changed by the heat treatment, and accordingly will receive little further consideration in this study.

Although the cellulosic purity of the pulps and the probable stability of the papers made from them were found to be related, it should be kept in mind that only a small amount of alum and no rosin size were used in the manufacture of the papers. Papers made from the same pulps may have different stabilities when quantities of these materials are added. The effect of these variables will be studied in the second part of this investigation.

The authors express their appreciation to H. F. Launer, E. E. Creitz, and R. W. Carr of this Bureau for assistance in the laboratory testing of the pulps and papers.

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STABILITY OF MOTION-PICTURE FILMS AS DETERMINED BY ACCELERATED AGING [1]

By John R. Hill [2] and Charles G. Weber

FOREWORD *

For some time past, many institutions—libraries in particular—have faced the problem of record storage in terms of space, cost, and stability. Among other subjects seriously considered with a view to a solution is the problem of photographically transferring records to a film base by what is commonly known as microphotography.

Custodians of records have accumulated experience in this field, but most of them hesitate to adopt a definite policy until more is known about the stability of film bases. The National Archives is especially interested owing to the great volume of Government records under its jurisdiction, duplicates of which in many cases are not available. This interest was increased when the Division of Motion Pictures and Sound Recordings was set up and efforts were made to preserve such material.

As a result of this interest the National Archives transferred money and personnel to the National Bureau of Standards with the understanding that the study then in progress on cellulose acetate film would be broadened to cover also cellulose nitrate film. Under this arrangement the work has moved forward rapidly and with gratifying results. The National Archives acknowledges the cooperation of the National Bureau of Standards and other participants in this work for their helpful contributions insofar as it has been a beneficiary.

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I. INTRODUCTION

Motion-picture films on a cellulose acetate base are being used as an inexpensive and convenient means of reproducing important records and for making original records for historical and other edu-

[1] This study was made with the assistance of a fund granted by the Carnegie Corporation to the National Research Council and a fund allotted by the National Archives, and with the advice of the following committee appointed by the National Research Council: Robert C. Binkley, American Council of Learned Societies and Social Science Research Council; John G. Bradley, National Archives; E. K. Carver, Eastman Kodak Company; H. T. Cowling, National Archives, representing Society of Motion Picture Engineers; V. B. Sease, du Pont Film Manufacturing Company; F. W. Willard, National Research Council; and H. M. Lydenberg, New York Public Library, chairman. The Film Preservation Committee of the Society of Motion Picture Engineers has been helpful also.

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cational purposes. The interest in films for such purposes has become widespread because of the great saving in library space and the greater availability of material afforded the research worker.

At the request of the American Library Association and other organizations concerned with the preservation of important records, an investigation of the chemical and physical properties of cellulose acetate films, relative to their stability, was undertaken. This work is a natural extension of the studies previously made on the preservation of records on paper. The American Library Association is interested in the stability of cellulose acetate film and information concerning the best practice with respect to its storage and use. The National Archives is interested in all problems involved in the preservation and use of both nitrate and acetate films because both types will be stored and used there. By coordinating the two projects, more rapid progress has been obtained than would have been otherwise possible.

II. MOTION-PICTURE FILMS STUDIED

A motion-picture film comprises a base of transparent sheeting, usually approximately 0.0055 inch in thickness, coated with an emulsion in the form of a thin layer of gelatin containing a silver compound extremely sensitive to the action of light. There are two types of film base in use, both being transparent cellulose esters: cellulose nitrate and cellulose acetate.

Cellulose nitrate sheeting is the base in the ordinary theater type of motion-picture film. It is essentially a mixture of cellulose nitrate and camphor, and is highly combustible. It ignites at low temperature and burns very rapidly, giving off large volumes of oxides of nitrogen which are poisonous. Cellulose nitrate is relatively unstable in any form. The base of the safety type of film contains cellulose acetate. This material is comparatively stable chemically, is not highly inflammable, and burns no more rapidly than ordinary paper. The samples used in this study were furnished by the three principal domestic manufacturers of motion-picture films and were said to be representative of current commercial products.

III. DESCRIPTION OF TESTS

The stability of the films was studied by determining the changes in their properties under accelerated aging. Various aging treatments were tried, consisting in: oven-aging at 100° C in dry air, a method of aging that had been found suitable for paper;[3,4] oven-aging with moisture provided by an open vessel of water in the oven; heating in a steam chest at 99° C; and oven-aging at 100° C with the film inside stoppered bottles containing saturated potassium sulphate solution, providing a relative humidity of 95 percent.

Both physical and chemical tests were used to measure the effects of accelerated aging. Any change in chemical properties should be reflected in the physical properties, and it is desirable to obtain a correlation between them. The physical property most sensitive to deterioration appears to be the flexibility, which can be measured by a folding test. The loss in weight on heating was also recorded. The

[3] BS J. Research 3, 476 (1929) RP107.
[4] Paper Trade J. 95, 28 (July 1932).

chemical testing comprised determinations for: acetyl content, and copper number on acetate film; flash or explosion temperature, and stability at 134.5° C for nitrate film; and acidity as pH, and relative viscosity of acetone solutions for both types of film.

The determination of acetyl content, undertaken to find whether the aging of acetate film resulted in loss of acetic acid, was discarded for the more direct determination of free acidity, developed in the film, as change in pH. The available methods of testing for acetyl content were not sufficiently sensitive to detect changes due to aging. Likewise, for nitrate film, the flash-point test was found to be unsatisfactory as a measure of stability, and the stability test at 134.5° C used by the Ordnance Department of the United States Army for testing guncottons was substituted. This latter test was found to be applicable to the testing of nitrate film as the time of reaction was affected

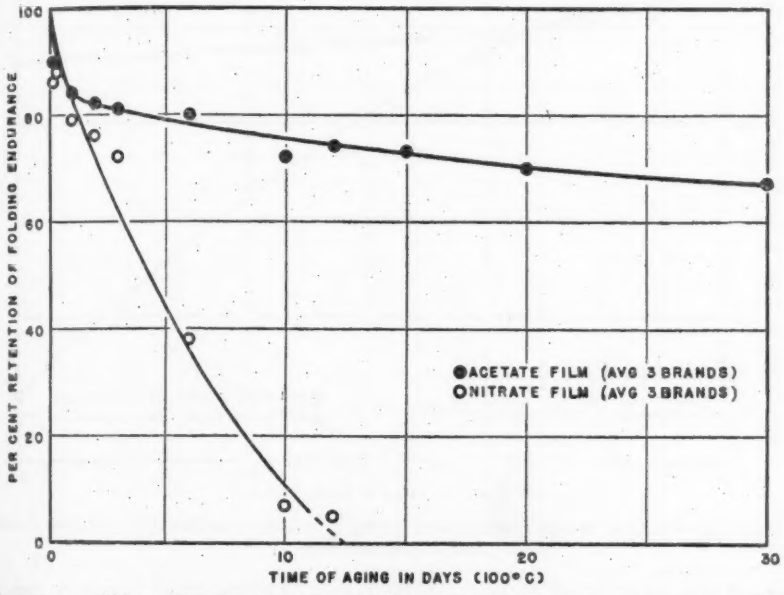

FIGURE 1.—*Effect of oven-aging on flexibility of cellulose acetate and cellulose nitrate motion-picture films.*

sharply both by changes due to artificial aging, and by those due to natural aging. All aging tests were made on samples of whole film, that is, film with the emulsion. Samples were taken from new films that had been exposed and processed by the manufacturers. These films gave a negative test for residual hypo.

IV. PHYSICAL PROPERTIES

1. FOLDING ENDURANCE

In studying the effect of accelerated aging on the folding endurance, two types of folding testers were tried; the MIT folding tester used for paper and the Pfund type of tester which is used by the Du Pont Film Manufacturing Corporation for films. The Pfund type was found to be somewhat more reliable as to reproducibility of results than the MIT type. Difficulty was encountered in the use of the latter

because a slight distortion of the film on aging caused edge cracks when it was folded over the jaw edges. The Pfund type folds without tension, forming a small loop not in contact with any metal edge. It appears to give a satisfactory measure of flexibility and, although hand-operated, the results are quite reproducible.

For measurements of folding endurance, test strips of film were cut 15 mm wide and about 75 mm long and aged at constant temperature for the required length of time. After aging, the strips were conditioned under the standard conditions of 65-percent relative humidity and 70° F before testing. Control strips were in all instances conditioned and tested under the same conditions. A 24-hour conditioning

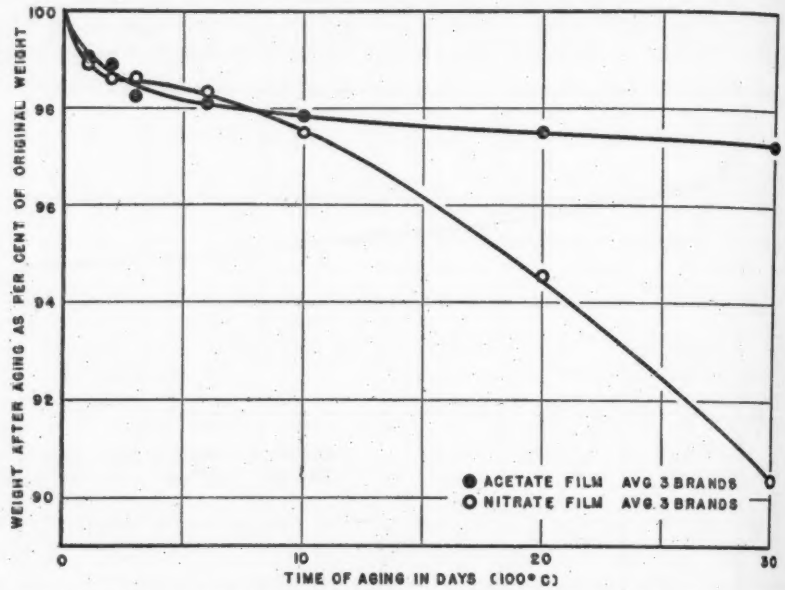

FIGURE 2.—*Loss in weight during oven-aging of cellulose acetate and cellulose nitrate motion-picture films.*

period was used in all cases as both types of films were found to reach practically constant weight within that time.

The results of ordinary oven-aging at 100 ±2° C on the folding endurance of cellulose acetate and cellulose nitrate film are shown in figure 1. The curves show average values for three brands each of acetate film and nitrate film. Both curves start with about the same slope and show a retention of between 80 and 85 percent of the original folding endurance after 24 hours' aging. On continued heating, the acetate film changed very slowly in folding endurance. After 30 days the average retention was about 67 percent, and after 150 days (not shown on curve) it was still about 50 percent of the original value. For the nitrate films, the loss in folding endurance continued at about the initial rate until all folding endurance was lost. After 10 days' heating, the folding endurance was zero for 2 brands and the third became zero after a few days of additional heating.

Moisture vapor in the oven practically doubled the loss in folding endurance for both types of film for a 72-hour period. It was not continued for longer periods because using open vessels of water in the oven resulted in extreme and uncontrollable changes in relative humidity. In the steam chest, nitrate film went to pieces rapidly, while in the case of the acetate the base became opaque and separated from the emulsion without loss of folding endurance. Upon heating this base in the oven, it again became transparent. The most consistent results with respect to effects on folding endurance were obtained with oven-aging in dry air.

2. LOSS IN WEIGHT

Oven-aging of film was found to be accompanied by a loss in weight that was not regained on reconditioning. This fact aids in understanding some of the results of oven-aging on folding endurance.

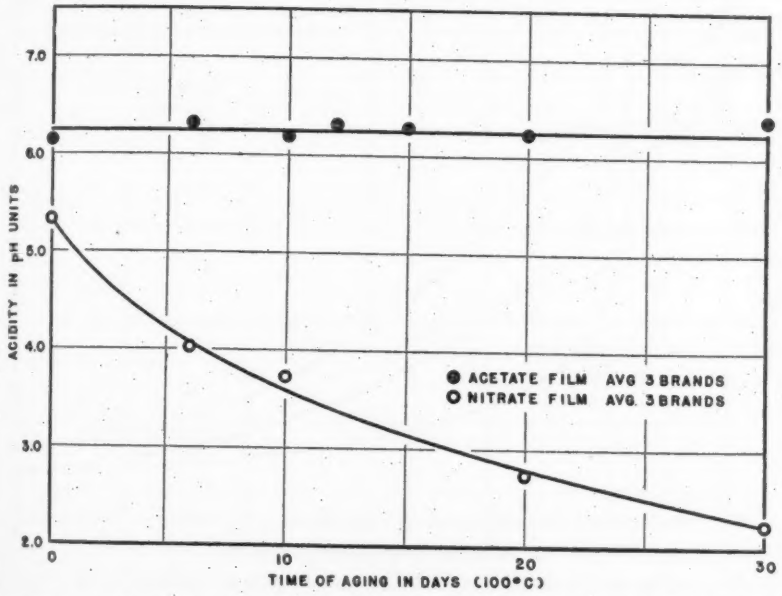

FIGURE 3.—*Effects of oven-aging on* pH *of cellulose acetate and cellulose nitrate motion-picture films.*

Weighed samples of film were aged for different periods and weighed again after conditioning for 24 hours. The final weights calculated as percentages of the original weights are shown on the curves in figure 2. The curves are similar for both types of film up to a period of about 6 days, but thereafter the loss in weight of acetate film is slight, while the nitrate continues to lose at a comparatively rapid and constant rate. These curves are similar in several respects to those for folding endurance. In each instance, the initial change was probably due to the loss of volatile substances, such as residual solvents and camphor in the case of nitrate film. On further aging, the slow change in the acetate film indicates greater stability.

V. CHEMICAL PROPERTIES

1. ACIDITY (pH)

Decomposition of cellulosic materials is usually accompanied by an increase in their acidity; hence measurements of pH were made to determine whether aging was accompanied by any increase in acidity. For this test, 1-g samples of film were weighed and after aging the base of the specimen was dissolved in 100 ml of acetone containing 10 percent by volume of water.[5] The pH of the solution was measured with a glass electrode. The results are shown in figure 3, in which the pH of the solution is plotted against the time of aging. The curve for acetate film shows some fluctuations, but no significant changes for any period of aging up to 30 days. On the other hand, the nitrate films showed a regular drop in pH from an average value

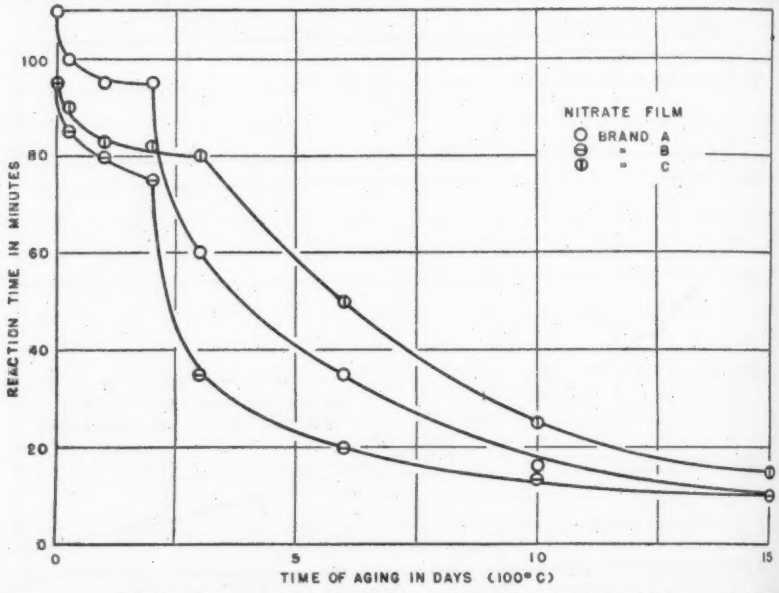

FIGURE 4.—*Effects of oven-aging of cellulose nitrate film on its stability at 134.5° C.*

of about 5.3 for new film to 2.3 after 30 days of aging. Correspondingly high acidity was found also in every test of old nitrate film that was visibly deteriorated as a result of natural aging.

2. STABILITY TEST OF NITRATE FILM

The stability test at 134.5° C,[6] used for testing pyrocellulose and guncotton, was found to be applicable to cellulose nitrate film. In this test, a 1-g specimen is placed in a closed tube with normal methyl violet paper inserted in the tube to about 2.5 cm above the test specimen. The time required at a constant temperature of 134.5° C for the gases given off from the specimen to change completely the color of the paper to salmon pink is observed. The effects of oven-aging

[5] T. K. Brownson and F. McCray, *The electrical conductivities of hydrochloric acid and potassium chloride in water and acetone-water mixtures.* J. Chem. Soc. **127**, 2923 (1925).
[6] U. S. Army Specification no. 50-14-3.

on the stability of nitrate film, as determined by this test, are shown in figure 4. The curves for the different commercial brands are alike in general characteristics, showing slow rates of change of stability for the first two days of heating, then sharp breaks in the curves followed by much more rapid loss of stability. Old film, visibly deteriorated by natural aging, usually had a reaction time corresponding to 10 to 15 days of oven-aging.

3. COPPER NUMBER

Some forms of degraded cellulose reduce copper from an alkaline solution of copper sulphate, and the amount reduced is considered a measure of the amount of such material present. In applying this

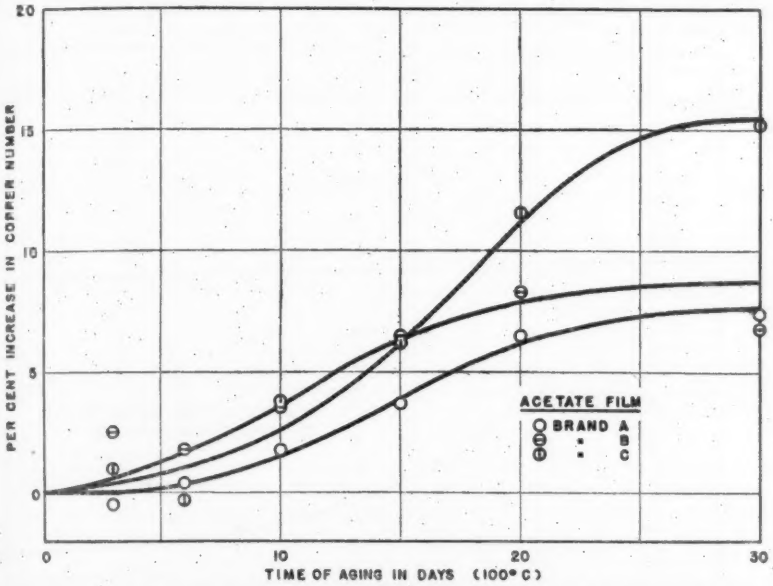

FIGURE 5.—*Effect of oven-aging on the copper number of cellulose acetate motion-picture film.*

test to films, the standard method [7] for testing the copper number of paper was used, except that the samples were prepared in the following manner. The film was dissolved in acetone, and the cellulose ester precipitated in hot water, washed, and dried. The resultant samples were in soft fluffy form comparable to the paper samples prepared by grinding. Both acetate and nitrate films were tried, but no figures were obtained for nitrate film because it dissolved completely in the alkaline copper sulphate solution.

The data on the copper numbers of three brands of acetate film are shown in figure 5. Four series were run on each brand. The reproducibility of results was not very good but, in each instance, there was an increase in copper number with aging. For 30 days of aging, the increases in copper number values were 7, 15, and 7 percent, respectively, an average of about 10 percent. Compared with the change

[7] TAPPI Standard T430m, Tech. Assn. of the Pulp and Paper Ind.

occurring in stable papers, this would be considered a small increase, indicative of relatively high chemical stability. The initial copper number values for the three brands of film averaged 3.2, which is considerably higher than for permanent paper. This is not surprising when the more drastic chemical treatment used in making the acetate film is considered. Hence, the two materials are not comparable on the basis of actual values, but rather on the rate of change on heating.

4. VISCOSITY

The relative viscosity of acetone solutions of the film base was found to be the most sensitive and reliable chemical test for following the deteriorative effects of aging on both acetate and nitrate films. The viscosity data are of special interest because of the excellent correlation between changes in viscosity and loss in folding endurance on

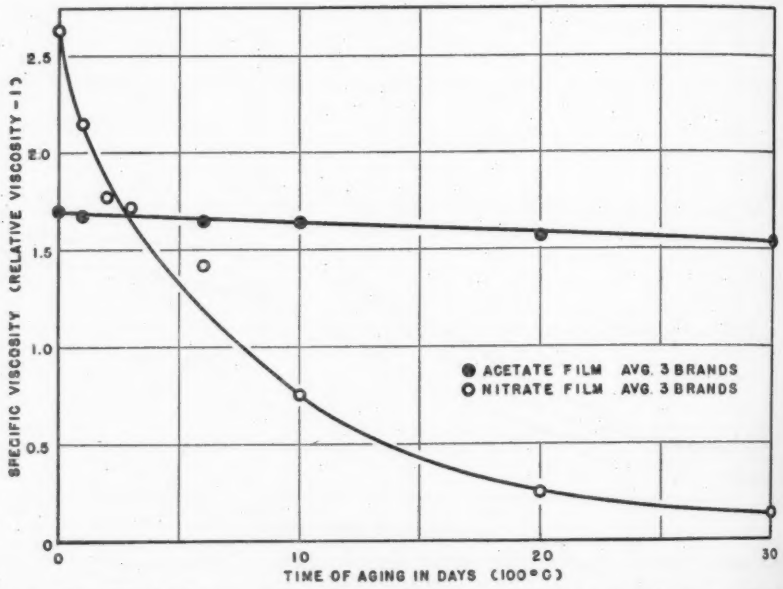

FIGURE 6.—*Effect of oven-aging on the viscosity of cellulose acetate and cellulose nitrate motion-picture films.*

aging. This good correlation between changes in physical and chemical properties indicates a sound basis for judging relative stability.

The molecular weight of substances with long-chain molecules is related to the viscosity of their dilute solutions, according to Staudinger,[8] by the following equation:

$$\eta_r - 1 = \eta_{sp} = K_m.c.M,$$

where η_r is the relative viscosity, which is the ratio of the viscosity of the solution to the viscosity of the solvent; η_{sp} is the specific viscosity as defined by Staudinger; K_m is a constant, c is the concentration in primary moles per liter of solution; and M is the molecular weight. From this equation it can be seen that for equally concentrated solu-

[8] H. Staudinger, Die Hochmolekularen Organischen Verbindungen (Berlin, 1932).

tions of the same K_m, the viscosity depends only on the molecular weight. Consequently, any break down in the molecular structure should result in a lowering of the viscosity.

The effect of accelerated aging on viscosity was determined by viscosity measurements before aging and after various aging periods. Specimens weighing 1.000 g each were used. The test was made by dissolving the film base away from the emulsion in acetone, making the solution up to 100 ml in a volumetric flask, and measuring the time of flow of the solution in an Ostwald viscosity pipette immersed in a constant-temperature water bath at 30 $\pm$.02° C. The product of the time of flow and density of the solution divided by the corresponding product for the solvent gives the relative viscosity.

The results of ordinary oven-aging in dry air are shown in figure 6. This shows specific viscosity plotted against time of aging. The

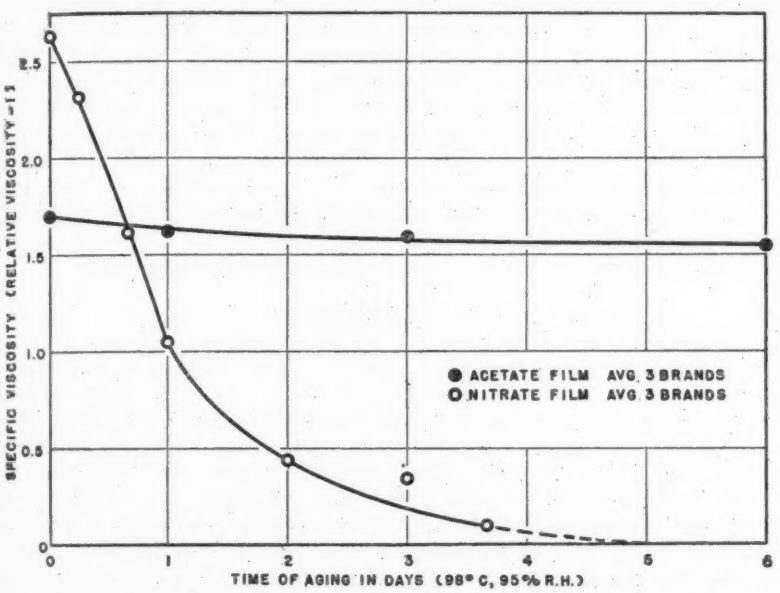

FIGURE 7.—*Effect of oven-aging with high relative humidity on viscosity of cellulose acetate and cellulose nitrate motion-picture films*

curve for acetate film shows very slow change. The decrease in specific viscosity for 30 days' aging was only from 1.70 to 1.54, or 9.4 percent. For the same time of aging, the nitrate film decreased from an average value of 2.63 to 0.14, which indicates a complete change in structure. Old nitrate film badly deteriorated from natural aging gave a viscosity corresponding to about 10 days of oven-aging.

In order to determine the effect of high humidity, samples of film were aged suspended over a saturated solution of potassium sulphate in a closed bottle. The temperature maintained in the bottle was 98$\pm$2° C, and at this temperature the relative humidity is 95 percent. The results are shown graphically in figure 7. Under these conditions, decomposition was more rapid for both types of film, but especially for the nitrate film. The high relative humidity resulted in hydrolysis with the formation of nitric acid, which greatly accelerated the reaction. The average time required for a 95-percent

decrease in viscosity was about 3 days, compared with 30 days for oven-aging in dry air. The decrease in viscosity of acetate film for 3 days of aging was 6.5 percent. This is a greater change than that for the same time of aging in a dry atmosphere (fig. 6) but is small compared with the change found for nitrate film, and indicates excellent stability even under these extreme conditions.

5. EFFECTS OF AGING ON GELATIN EMULSION

Ordinary oven-aging in dry air had no effect on the gelatin emulsion of acetate films as far as could be observed. The aging at 100° C with 95-percent relative humidity resulted in some softening of the emulsion and a tendency of the emulsion to separate from the base. The first visible evidence of deterioration of nitrate film with natural aging is a discoloration and softening of the emulsion. Tests of the emulsions from such films showed that oxidation, as indicated by relatively high ammonia nitrogen content, and hydrolysis, as indicated by relatively high amino nitrogen content, had both taken place. Results of tests on the emulsion of oven-aged film showed that the oxidation was increased from 0 to 0.89 percent and hydrolysis from 1.89 to 3.90 percent by oven-aging. This apparently results from contact with the products of decomposition of cellulose nitrate as there was correlation between the acidity of the film and condition of the emulsion. Hence, the softening of the emulsion of nitrate films often observed after natural aging may be said to be an indirect result of the decomposition of the cellulose nitrate film base.

VI. SUMMARY

On the basis of the test data, the cellulose acetate type of safety film appears to be a very stable substance. It is a comparatively new material on which no natural aging data are available. However, data on the relative resistance to accelerated aging of the acetate film, nitrate film, and permanent record papers are very favorable to the acetate film. A specification, proposed by Scribner,[9] for permanent record paper of the highest quality, requires a retention of folding endurance of 85 percent after heating 72 hours at 100° C. Acetate film retained 50 percent after 150 days at the same temperature. Nitrate film, known to be relatively impermanent, had no folding endurance after 10 days of heating.

The relatively high chemical stability of acetate film is shown by the fact that aged samples showed no increase in acidity, whereas nitrate film became distinctly acid. For permanent record paper, the copper number must not be greater than 1.0 nor increase more than 0.5 when heated for 72 hours. The average value of the copper number of cellulose acetate was 3.2. This is higher than for permanent record paper as would be expected as a result of the chemical treatment undergone in acetylation of the cellulose, but on heating for 72 hours at 100° C cellulose acetate showed an average increase of less than 0.5.

The best evidence of the high stability of acetate film is furnished by results of viscosity measurements. When heated for 72 hours at 100° C, the specific viscosity decreased about 2 percent, and after 30

[9] Trans. Am. Soc. Mech. Engrs. 52, [PI] 21 (August 1930).

days of aging only 9 percent. With nitrate film, the decrease was 35 percent in 72 hours and 95 percent after 30 days of aging.

While it is not possible to predict the life of acetate film from these results, the data show that the chemical stability of the film, with respect to oven-aging, is greater than that of papers of maximum purity for permanent records. On the basis of this comparison, cellulose acetate motion-picture film appears to be very promising for permanent records.

Acknowledgments are made to J. E. Gibson and Meyer Reiss, Research Associates, for assistance in this investigation while assigned to this Bureau by the Division of Motion Pictures and Sound Recordings, National Archives.

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SOME PHYSICAL PROPERTIES OF ISOPRENE

By Norman Bekkedahl, Lawrence A. Wood, and Mieczysław Wojciechowski [1]

ABSTRACT

Isoprene (2-methyl-1,3-butadiene) has been prepared in a state of high purity. Physical properties determined on the freshly purified sample were as follows, boiling point, 34.076 ±.003° C; change of boiling point with change of pressure: $\frac{dt}{dP}$=0.0382° C per millimeter of mercury; freezing point, −146.8 ±.2° C; density at 20° C, 0.6805 ±.0001 g/ml; refractive index at 20° C, 1.42160 ±.00005. The molecular refraction was calculated to be 25.39. The volume expansivity was measured over the entire range of temperature between the freezing point and normal boiling point, giving the following equations:

$$V=V_0(1+1.393\times10^{-3}t+2.79\times10^{-6}t^2+4.31\times10^{-9}t^3-5.60\times10^{-12}t^4)$$

$$\rho=0.7002-0.9754\times10^{-3}t-0.592\times10^{-6}t^2+0.525\times10^{-9}t^3+9.66\times10^{-12}t^4,$$

in which V and ρ are the volume and density, respectively, at the temperature t, and V_0 the volume at 0° C. From the Clausius-Clapeyron equation the latent heat of vaporization at the normal boiling point was calculated to be 25.9 ±.3 kj/mole. The refractive index at any temperature from about 0° C to the boiling point may be calculated from the equation

$$n_D=1.43472-0.656\times10^{-3}t.$$

On standing, the isoprene was found to undergo a transformation, presumably oxidation and polymerization, as was indicated by changes in purity, boiling point, density, and refractive index.

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I. INTRODUCTION

Isoprene (2-methyl-1,3-butadiene) has been for many years a substance of very considerable interest in the study of rubber, since it has been shown to be the fundamental unit in the constitution of the rubber hydrocarbon. Isoprene polymerizes to form a product which

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is chemically more closely related to natural rubber than any other synthetic product [9, 20, 33, 35, 48, 53, 56].[2] Furthermore, the destructive distillation of natural rubber yields as its two major products isoprene and dipentene (*dl*-1-methyl-4-isopropenyl-1-cyclohexene) in amounts far exceeding those of any other constituents [4, 30, 56]. Aside from its relation to rubber, isoprene is of interest because it is thought to be the basic substance in the natural synthesis of the terpenes and to play an important role in the formation of plant cells [3, 8, 13, 49, 50, 54].

An investigation of the chemical thermodynamics of rubber now in progress at the Cryogenic Laboratory of this Bureau includes a study of isoprene and its relationship to rubber. Measurements of heat capacity and heat of combustion are at present being made on isoprene for the purpose of calculating its entropy. A report covering these results is now being prepared. Similar measurements for rubber have already been reported [5].

Since samples of high purity were desired for this work, care was taken in the preparation and purification of the isoprene, and the resulting product is thought to represent an improvement in purity as compared with isoprene prepared by previous investigators. Furthermore, not all workers had realized the importance of working with freshly purified samples. Also it is now possible to take advantage of recent important improvements in the technique of measuring physical properties, especially boiling point and related properties. In view of the wide divergence of values for many of the commonly measured physical properties, as reported in the literature, it seems worth while to report the values here obtained with samples of high purity.

II. PREPARATION AND PURIFICATION OF SAMPLE

The isoprene was made by the cracking of dipentene vapor by means of the "isoprene lamp" method of Harries and Gottlob [22] as modified by Whitby and Crozier [55]. About 5.5 liters of crude isoprene was prepared which had a yellow color and possessed a sharp odor. It was then subjected to successive distillations. The vacuum-jacketed column used was about 140 cm in height and included 40 bulbs with ball valves and side tubes, according to the design of Świętosławski [39, 40]. The column head included a dephlegmator and condenser with take-off so arranged that the reflux ratio could be adjusted by means of drop-counters. For the isoprene distillation a 15 to 1 ratio was generally maintained. Temperature changes were read to the nearest 0.001° C by means of a Beckmann-Świętosławski mercury thermometer [41] immersed in a mercury well surrounded by vapor rising from the dephlegmator. Corrections in the distilling temperature of the isoprene were made for changes in barometric pressure by simultaneous observations of the boiling point of pure water in a barometric ebulliometer.

Three successive distillations were made, with a reduction of charge in each case to include only the most nearly constant-boiling part of the previous distillation. Isoprene was evidently present in far greater amounts than any other substance. The impurities were

[2] The numbers in brackets here and elsewhere in the text refer to the numbered references at the end of this paper.

very largely materials of boiling points lower than that of isoprene, some of them condensing only at the temperature of solid carbon dioxide. In the early fractions of the first distillation, water was distilled over in small amounts as a separate phase. When the first distillation was continued above the boiling point of isoprene, no significant approach to constancy of boiling point was obtained below 176° C, the approximate boiling point of dipentene. It was therefore concluded that the cracking process had yielded practically no substances with boiling points between those of isoprene and dipentene, and that the crude isoprene had contained some unchanged dipentene.

The third and final distillation yielded 200 ml of a product distilling within a range of 0.01° C. The sample was colorless and possessed only a slight odor. This fraction was thoroughly mixed and different portions were used immediately in the determination of physical properties, several measurements being performed simultaneously.

III. PHYSICAL PROPERTIES

A number of previous observers have noted that isoprene on standing for months or years at room temperature under atmospheric conditions will oxidize and polymerize [1, 11, 12, 26, 44, 55]. For this reason the physical properties here reported were determined as soon as possible after the final distillation. With the exception of the freezing point and expansivity, all measurements were made within 5 hours after the end of the final distillation. The sample used in the freezing-point determination had been kept in a refrigerator at about 8° C for 2 days, while that used in determining the expansion was several weeks old.

The expansivity, however, is thought to change only slightly with change in purity. In order to obtain some idea of the rate of polymerization, a sample which had been kept at 8° C for 2 months was distilled, and a solid residue amounting to less than 0.5 percent of the weight of the sample was obtained.

1. DEGREE OF PURITY

Świętosławski [42] has set up for comparative purposes an arbitrary scale for the degree of purity of liquids. This scale is based on the measurement of Δt, the difference between the temperature of the boiling liquid and the temperature of the condensing vapor as determined in a differential ebulliometer of standard dimensions. For a pure substance Δt is zero, and increases with increased concentration of impurities.

The freshly prepared sample of isoprene from the third distillation was found to have a Δt of 0.002° C. This value falls within the limits of the fifth or highest degree on the purity scale (range from 0.000 to 0.005° C). A sample of isoprene from the previous distillation was found to have a Δt of 0.006° C. Its purity then was of the fourth degree (range from 0.005 to 0.020° C). This sample was left in the ebulliometer at room temperature for 2 weeks. At the end of this time its Δt value had increased to 0.028° C, and its purity had decreased to the third degree (range from 0.020 to 0.050° C). This increase in Δt is direct confirmation of the expected decrease in purity brought about by oxidation and polymerization of the isoprene. Changes with time in other physical properties as mentioned below are other evidences of change in the material.

2. BOILING POINT AND ITS RELATION TO PRESSURE

The normal boiling point of isoprene was determined in the ebulliometer used for the purity determination, following the comparative method of Świętosławski [43]. According to this procedure a second ebulliometer containing pure boiling water is connected, together with the first ebulliometer, to a closed system in which the pressure can be adjusted. Determinations of the boiling point, by observing the temperature of the boiling liquid in equilibrium with the vapor, were made for both liquids under at least three different pressures, including values both above and below 760 mm of mercury. The temperatures were measured with a Mueller [31] type of Wheatstone bridge and a resistance thermometer designed for precise temperature measurements [29], and calibrated in accordance with the procedure for the International Temperature Scale [10].

In order to obtain the normal boiling point of isoprene from the observations it was merely necessary to find the boiling point of isoprene under the pressure at which the boiling point of water would be exactly 100° C, since that pressure is exactly 760 mm by definition of the temperature scale. This procedure avoids the loss of precision inherent in the corrections to be applied to the readings of a mercury barometer.

For a sufficiently small range of pressures near the normal boiling points the relation between t_s, the boiling point of an organic substance, and t_w, the boiling point of water under the same pressure, can be represented by a function of the second degree; hence its derivative, $\frac{dt_s}{dt_w}$, changes linearly with change of pressure when this pressure is defined by the boiling point of water [58]. It was found that the quotient of finite increments, $\frac{\Delta t_s}{\Delta t_w}$, evaluated at the midpoints of several small intervals, changed only about 0.2 percent for a 2° C change of t_w. The ratios $\frac{\Delta t_s}{\Delta t_w}$ were evaluated at the midpoints between t'_w and t_w, and t''_w and t_w, respectively; t_w being a measurement close to 760 mm pressure, t'_w below, and t''_w above this pressure. The derivative $\frac{dt_s}{dt_w}$ at 100.000° C was obtained by interpolation. These values are given in table 1. The normal boiling point, t_B, is then calculated [57] from the observed values of t_s and t_w by the equation

$$t_B = t_s + \frac{dt_s}{dt_w}(100.000 - t_w)$$

The estimated probable error in the normal boiling point, 34.076° C, based on three determinations of this kind, is ±0.003° C.

TABLE 1.—*Degree of purity, boiling point, and change of boiling point with change of pressure for several samples of isoprene*

Δt[a]	Degree of purity	$\frac{dt_s}{dt_w}$[b]	Boiling point of water	$\left(\frac{dt}{dP}\right)_s$[c]	Normal boiling point of isoprene sample
°C			°C	°C/mm	°C
0.028	Third			0.0383	34.124
.006	Fourth				34.102
.002	Fifth	[d] 1.0367 [f] 1.0359 [h] 1.0338	[e] 100.720 [g] 100.000 [i] 97.988	.0382	34.076

[a] Difference between the boiling temperature of isoprene and its condensation temperature in a differential ebulliometer of standard dimensions.
[b] Ratio of the change in boiling point of isoprene to that of water for the same change in pressure.
[c] Change of boiling point of isoprene per millimeter change of pressure at 760 mm.
[d] At midpoint between t_s and t'_s.
[e] $\frac{t'_w+t_w}{2}$.
[f] Interpolated value.
[g] Defining 760 mm pressure.
[h] At midpoint between t'_s and t_s.
[i] $\frac{t'_w+t_w}{2}$.

The value of $\frac{dt}{dP}$, the change of boiling point of isoprene with change of pressure at 760 mm of mercury, was obtained by multiplying the value of the derivative $\frac{dt_s}{dt_w}$ at 760 mm by 0.369, which is the value in degrees per millimeter for the change of boiling point of water at 760 mm [32]. The value for isoprene was thus found to be 0.0382° C per millimeter of mercury.

Table 1 also shows the data and results of these determinations. For the purpose of comparison some values are also given for samples of lower purity. Higher boiling points and larger values of $\frac{dt}{dP}$ are characteristic of less pure samples.

3. FREEZING POINT

The freezing point of isoprene was measured in accordance with the procedure of Mair [28], using apparatus essentially similar to that described by him.

The isoprene was contained in a double-walled glass tube, the inner space between the walls being evacuated. Temperatures were measured with the same platinum resistance thermometer used for the boiling-point determination. Mechanical stirring with a spiral wire surrounding the thermometer and operated by an electric motor was continued throughout the determination.

The data for the freezing- and melting-point determinations are plotted in figure 1. The freezing point, determined as the temperature of the intersection of the freezing curve with the normal cooling curve, agrees with the melting point determined in a similar manner from the melting and the normal warming curves. The estimated error in the value −146.8° C is thought not to exceed ±.2° C. The variation obtained in repeated observations on a single sample was considerably less than 0.2° C but was of this order between different

samples. Preliminary results of somewhat less precise melting-point determinations made in the course of heat-capacity measurements on a different sample using quite different apparatus and technique gave a value of −146.6° C.

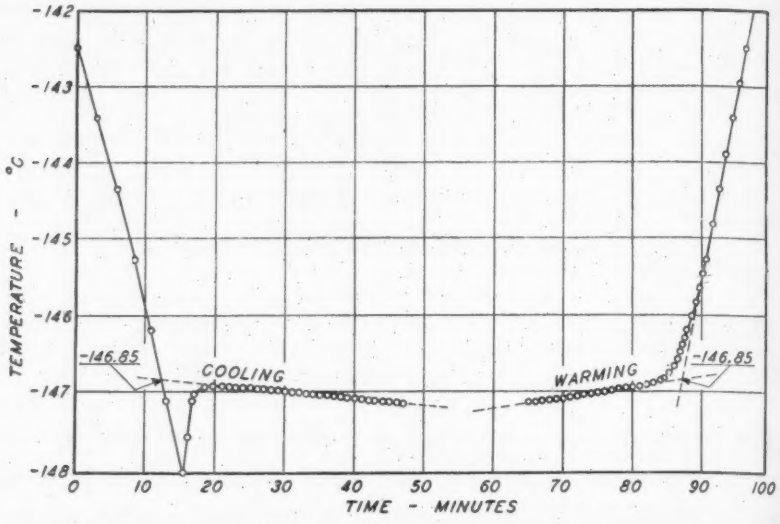

FIGURE 1.—*Temperature measurements made on an isoprene sample passing through the liquid-solid transition, both cooling and warming.*

4. VOLUME EXPANSIVITY

The volume expansivity, or temperature coefficient of volume expansion, $\frac{1}{V}\frac{dV}{dt}$, in which V is the volume at the centigrade temperature t, was determined by dilatometer measurements extending from

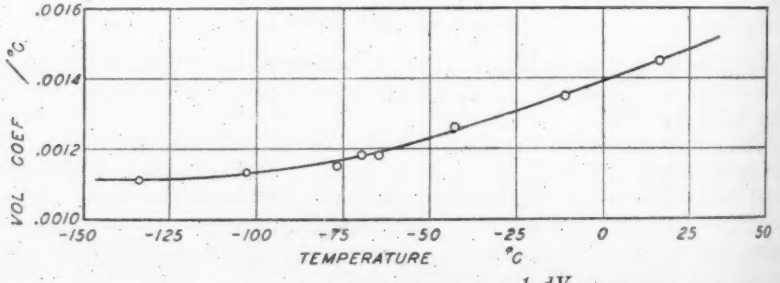

FIGURE 2.—*Relation between the volume expansivity,* $\frac{1}{V}\frac{dV}{dt}$, *of liquid isoprene and temperature.*

temperatures near the freezing point almost to the boiling point. The dilatometer, made of low-expansivity glass, had a bulb with a volume of 22.31 ml capacity, joined to a capillary about 40 cm in length with an average volume of 0.02276 ml per centimeter. A temperature range of about 20° C was covered in each run. For each run there was plotted a graph of the height of the liquid in the capillary as a

function of the temperature. The temperature range was so small that no significant deviations from linearity over a single run could be observed. From the slope of the graph and the dilatometer dimensions the expansivity at the mean temperature of each run was calculated. These values have been plotted in figure 2, each point representing a separate run.

Four terms were necessary in a power series in order to express the expansivity to within 1 percent over the whole range of temperature, as given in the following equation:

$$\frac{1}{V}\frac{dV}{dt}=-\frac{d\rho}{\rho dt}=1.393\times10^{-3}+3.63\times10^{-6}t+5.35\times10^{-9}t^2-38.8\times10^{-12}t^3$$

For temperatures above $-100°$ C this equation yields values agreeing with the observed expansivity to better than 0.5 percent. An integration of the preceding equation, together with the expansion of an exponential, leads to the following equation:

$$V=V_0(1+1.393\times10^{-3}t+2.79\times10^{-6}t^2+4.31\times10^{-9}t^3-5.60\times10^{-12}t^4)$$

in which V_0 is the volume at 0° C.

5. DENSITY

The density of a sample of the purest isoprene was determined by E. R. Smith of this Bureau, using a quartz picnometer of a type previously described [36, 51]. The temperature was thermostatically controlled at 20.00 ±.02° C. Since the picnometer had a capillary of about 0.1 mm diameter and was closed with a ground-glass joint, the evaporation correction, made by extrapolation of the observed change of weight with time, was very small. The value actually obtained for the density was 0.68053 g/ml. In view of the uncertainties caused by the change of the material with time, as noted below, the value is rounded off and reported as 0.6805 ±.0001 g/ml. From the density of the isoprene at 20° C and the expansivity data, the following equation may be derived for the density, ρ, of liquid isoprene at any temperature, t:

$$\rho=0.7002-0.9754\times10^{-3}t-0.592\times10^{-6}t^2+0.525\times10^{-9}t^3+9.66\times10^{-12}t^4.$$

After storage for 24 hours at 8° C the value obtained for the same sample at the same temperature had risen from 0.6805 to 0.6808 g/ml. Values on the two succeeding days were 0.6814 and 0.6819 g/ml, respectively. This continuous rise in density is further evidence of the change brought about by oxidation and polymerization.

6. CALCULATION OF HEAT OF VAPORIZATION

The Clausius-Clapeyron equation can be used for the calculation of the latent heat of vaporization of isoprene when the previously determined constants are used together with the specific volume of the vapor at the boiling point. Measurements of the specific volume have not been made, but an approximate value can be calculated. Normal pentane and isopentane are the liquids most similar to isoprene for which data on critical temperatures and pressures are available. For each of these at the boiling point the "reduced temperature" [27], or ratio of temperature to critical temperature, is about 0.65. Also for each of these at the normal boiling point the "reduced pressure",

or ratio of pressure to critical pressure, is about 0.030. Since there is very little difference in the "reduced" states at the boiling point for similar organic compounds, these may be presumed to be the approximate values for isoprene at its boiling point.

Lewis [27] has recently published graphs, applicable to any hydrocarbon with more than three carbon atoms per molecule, which yield as a function of the "reduced" states the value of μ, defined as PV/RT, in which P and V are respectively the pressure and volume of 1 mole of vapor, R is the universal gas constant, and T the absolute temperature. For the above values of the "reduced" temperature and pressure, Lewis' graph indicates a value of 0.96 for μ. In other words, at the boiling point the specific volume of isoprene vapor is 96 percent of the specific volume of an ideal gas of the same molecular weight and at the same temperature and pressure. (Direct observations on n-pentane and isopentane at their boiling points, yield values of μ within 1 percent of 0.96.) The specific volume of an ideal gas of the same molecular weight as isoprene at 34.076° C and under a pressure of 760 mm is 371 ml/g. The specific volume of isoprene vapor under the same conditions is therefore 356 ml/g.

In the Clausius-Clapeyron equation

$$L=\frac{T(V_v-V_l)}{\frac{dt}{dP}}$$

L is the latent heat of vaporization of 1 g of liquid; T, the boiling point, 307.2° K; V_v, the specific volume of the vapor, 356 ml/g; V_l, the specific volume of the liquid calculated from the previous values for density and expansivity, 1.5 ml/g; and $\frac{dt}{dP}$, the rate of change of boiling point with change of pressure as previously measured, 0.0382° C per millimeter (or 28.7×10^{-6} °C per dyne/cm^2). The latent heat of vaporization of isoprene at the normal boiling point is thus calculated to be 380 j/g (90.8 cal/g) or 25.9 kj/mole (6.17 kcal/mole). Because of the uncertainty in the value of the specific volume of the vapor the estimated probable error in the calculation is ±1 percent.

The Bingham-Nernst modification [6] of Trouton's rule is

$$\frac{L_m}{T_B}=17+0.011T_B,$$

in which L_m is the molal latent heat of vaporization in calories, and T_B the absolute temperature of the boiling point. The right-hand member of the equation has the value 20.4, and the left-hand member 20.1. The rule in this form appears to be valid for isoprene within the limits of precision of determination of the heat of vaporization. This is taken as evidence that isoprene in the liquid form is not associated.

7. REFRACTIVE INDEX AND MOLECULAR REFRACTION

Measurements of refractive index at temperatures from 9 to 30° C were made with a water-jacketed Abbe refractometer (Valentine model) calibrated with distilled water. The values obtained are plotted in figure 3, from which the refractive index at 20° C is found to be 1.42160 $\pm$.00005, and the change with change in temperature

-0.656×10^{-3} per degree centigrade. Therefore, the index of refraction, n_D, at temperature, t, is

$$n_D=1.43472-0.656\times10^{-3}t.$$

This equation is applicable for liquid isoprene at least over the range from 9 to 30° C and probably over a wider range. The refractive indices of fractions boiling both below and immediately above the purest isoprene were lower than that of the isoprene. The property is, however, not sensitive to very small amounts of impurities having boiling points near that of isoprene, since the third distillation, which lowered Δt from 0.006 to 0.002° C, raised the refractive index only by about 0.00001.

Oxidation and polymerization of the isoprene on standing, however, brought about progressive increases in refractive index. For the first

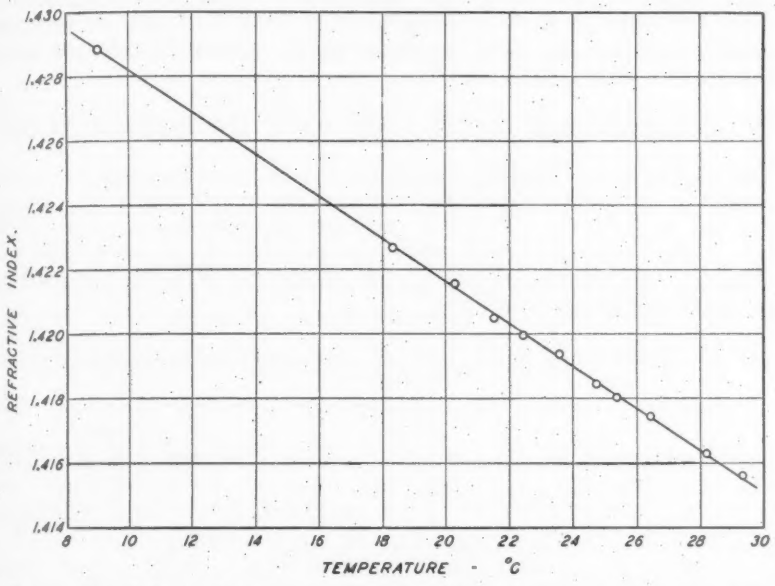

FIGURE 3.—*Relation between the refractive index of isoprene and temperature.*

few days the daily changes were of the order of 0.0002. Later the rate of increase became considerably less, and rather variable. At the end of 2 months the total increase was about 0.00450, and the material had become so lacking in homogeneity that further measurements were impossible.

The molecular refraction is often calculated by summing up the refractions of the individual atoms and adding a certain quantity for the "exaltation" due to double bonds or other special features of the structure. In the present case, however, no precise calculation is possible because the exaltation due to the conjugated double bond varies considerably from one compound to another. From the Lorenz-Lorentz formula, using the refractive index and density values as determined in this investigation, the molecular refraction is computed to be 25.39. By taking this value for the molecular refraction, and 2.490 and 1.066 for the atomic refractions of carbon and hydrogen, respectively, as reported by Świętosławski [38], the exaltation due to the conjugated system in isoprene is 4.41. This is not greatly different

from 4.32 for the conjugated system in 2,3-dimethyl-1,3-butadiene and 3.98 for chloroprene (2-chloro-1,3-butadiene).

The molecular refraction is commonly thought to be practically independent of temperature over moderate ranges. If this is true, differentiating the Lorenz-Lorentz equation gives in the resulting equation a relation between the change of refractive index with change of temperature and the expansivity.

$$\frac{dn}{dt}=-\frac{(n^2+2)(n^2-1)}{6n}\left(\frac{dV}{Vdt}\right).$$

At 20° C the observed expansivity is 1.467×10^{-3} per degree centigrade and the observed refractive index is 1.42160. These quantities yield a numerical value of 0.705×10^{-3} for the right-hand member of the above equation. This is to be compared with 0.656×10^{-3}, the directly observed value of the left-hand member. This agreement is only fair, but it is of interest to note that both values are considerably higher than those given for most organic liquids, for which the average is about 0.45×10^{-3}.

IV. COMPARISON WITH PREVIOUS INVESTIGATIONS

The boiling point, density, and refractive index of isoprene have been determined by many investigators, and the more significant results are given in table 2. For the purpose of comparison, the boiling points have been converted, wherever possible, to those at 760 mm pressure. Also the original values of density and refractive index have been converted to those at 20° C.

TABLE 2.—*Comparison of the data of various investigators on some physical properties of isoprene*

Observers	Year	Reference number	Boiling point at 760 mm	Density at 20° C	Refractive index at 20° C	Freezing point
			°C	g/ml		°C
Williams	1860	[56]	37 to 38[a]	0.6811		
Tilden	1882	[47]	34 to 35[a]			
Gladstone[b]	1886	[18]		.6681	1.4028	
Thorpe and Jones	1893	[45]	35.5 to 36.1[a]	.6714		
Thorpe and Rodger	1894	[46]	35.5 to 37.0[a]			
Perkin	1895	[34]	36	.6717		
			36 to 37	.6696		
Ipatiew[c]	1897	[24]	32 to 33[a]	.6722	1.40646	
Euler	1897	[16]	33 to 39[a]			
Blaise and Courtot	1906	[7]	36[a]			
Harries and Gottlob	1911	[22]	35 to 37[a]			
Harries	1911	[21]	30 to 37[a]	.676	1.41205	
			36 to 37[a]	.6800	1.42333	
			35.5 to 36.0[a]	.6803	1.42019	
Lebedew and Skawronski	1913	[26]	34.5 to 35.0	.6803	1.42207	
Kucherov	1913	[25]		.6803		
Harries	1914	[19]	33.7 to 33.9	.6832	1.42387	
Steimmig	1914	[37]	33.5 to 34.0[a]	.6760		
Aschan	1915	[2]	34.1 to 34.6	.6811	1.41540	
Enklaar	1916	[15]				"About −120 °C"
Enklaar	1916	[14]	33.9 to 34.4	.6809	1.41786	
Waterman and van Westen	1929	[52]	34.4 to 34.9	.6806	1.4194	
Conant and Tongberg	1930	[11]	36 to 38[a]	.68		
Heisig	1931	[23]	33.7 to 34.1			
Farmer and Warren	1931	[17]	34.4 to 35.8	.6828	1.42093	
Whitby and Crozier	1932	[55]	34.0 to 34.5			
Bekkedahl, Wood, and Wojciechowski	1936		34.076	.6805	1.42160	−146.8

[a] Atmospheric pressure not recorded.
[b] Measurements made by Harries. See reference [21].
[c] Sample of isoprene obtained from Tilden.

Because of inadequate knowledge of the purity of the samples of previous workers it is difficult to make a critical evaluation of the importance of their measurements. Incomplete removal of low-boiling impurities would be likely to lead to low values of the boiling point, density, and refractive index; oxidation and polymerization, on the other hand, to lead to high values. Almost all previous determinations of the boiling point have been observations of the range of temperature during distillation, and the values obtained depend greatly on the rate of distillation as well as the purity of the substance distilled, and give in most cases the condensation temperature. With such a low-boiling liquid superheating of the vapor is very probable, except in apparatus especially designed to avoid it.

The only freezing point determination recorded in the literature appears to be that of Enklaar [15], who made visual observations of a small sample attached to a pentane thermometer. The resulting value, given as "about −120° C", is considerably higher than that here obtained. Enklaar was unable to observe any distinct melting point.

The thermal expansion of isoprene was measured by Thorpe and Jones [45] in 1893 over a range of temperature from 0 to 32.6° C. The volume relation is given as $V=V_0(1+1.4603\times10^{-3}t+0.99793\times10^{-6}t^2+56.0149\times10^{-9}t^3)$. The coefficient of t is about 4 percent higher than the value here reported. The other coefficients show little correlation, probably because of the difference in the ranges of temperature involved.

Perkin [34] determined densities of his isoprene samples at various temperatures from 4 to 25° C. From these values an expansivity of 1.43×10^{-3} is obtained for a temperature of 12° C. This is in very good agreement with the value 1.437 for the same temperature as calculated from the equation determined in this investigation.

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RESEARCH PAPER RP952

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DIFFERENCES IN LIMES AS REFLECTED IN CERTAIN PROPERTIES OF MASONRY MORTARS

Lansing S. Wells, Dana L. Bishop, and David Watstein

ABSTRACT

A survey was made of commercial quicklimes and hydrated limes with respect to some physical properties of importance to their use in mortars. Measurements of soundness, plasticity, and flow after suction were made on putties prepared from the quicklimes and hydrated limes and flows after suction were measured on cement-lime mortars prepared from the lime putties. It was found that the properties of the different limes varied widely. Flows after suction of lime mortars were roughly proportional to the plasticities of the lime putties. The properties of a lime were found to be more important than the proportions of lime used in preparing cement-lime mortars having high flows after suction.

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I. INTRODUCTION

Considerable attention has been paid to the effect of proportioning the constituents of cement-lime mortars upon the properties of the mortars, often with too little consideration of the differences in the properties of the constituents. The investigation herein described pertains primarily to differences in the properties of lime putties made from various limes and the relation to the differences in the resulting properties of lime and cement-lime mortars containing these putties.

II. MATERIALS

1. LIMES

The investigation included 43 limes, representing commercial products from various parts of the United States. These samples consisted of 19 pulverized quicklimes and 24 hydrated limes. The

quicklimes included 15 classed as high-calcium limes and 4 as dolomitic. The hydrated limes included 17 high-calcium and 7 dolomitic limes. The authors are indebted to the National Lime Association for cooperation in securing many of these samples.

2. CEMENTS

Two cements were used; a typical portland cement with a specific surface of 1,750 cm^2/g as determined with the Wagner turbidimeter,[1] and a high-early-strength cement with a specific surface of 2,770 cm^2/g.

3. SAND

Clean Potomac River mortar sand was used in all tests of mortars. The sieve analysis of this sand was as follows:

U. S. Standard Sieve no.	Sand passing (%)
4	100. 0
8	99. 4
16	94. 4
30	75. 2
50	14. 0
100	1. 0
200	. 5

III. TESTS AND RESULTS

1. LIMES

(a) SOUNDNESS

Both the hydrated limes and pulverized quicklimes were tested for soundness according to the procedure given in the Tentative Methods of Physical Test for Limestone, Quicklime, and Hydrated Lime, ASTM designation: C 110–34T.[2] This method consists essentially in steaming (120–lb/in.^{2} pressure) specimens made of two parts of lime-putty (whether made from quicklime or hydrated lime) and one part of quick-setting calcined gypsum. Under the condition of the test, particles in the lime which might under ordinary atmospheric condition require months or years to produce "pits" or "pops" in a plastered surface, are so accelerated in their hydration with consequent expansion that crater-like holes are produced in the test specimens in a relatively few minutes. Tests of panels made in the laboratory have shown good agreement between the actual development of pops and results of the autoclave test.[3]

All hydrated limes were made into stiff putties and allowed to soak, samples being taken at the end of 1 day and 3 days, respectively, for determination of soundness. The pulverized quicklimes were slaked in such a manner that the reaction progressed at or near the boiling point of water resulting in the formation of stiff putties, samples of which, in turn, were also soaked for periods of 1 day and 3 days before testing for soundness.

The results given in table 1 show that 7 of the 24 hydrated limes and 8 of the 19 pulverized quicklimes gave putties classified as unsound after soaking 1 day. At the end of 3 days of soaking putties from 4 of the hydrated limes and from 4 of the quicklimes were unsound.

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TABLE 1.—*Results of soundness and plasticity determinations on putties made from hydrated limes and quicklimes soaked 1 day and 3 days, together with "flow after 1-minute suction" of lime-sand mortars made from these putties*

Lime no.	Soundness at end of—		Plasticity—			"Flow after suction" of lime-sand mortars (1:6 by wt) after 1 minute
	1 day	3 days	At end of 1 day	At end of 3 days	At time of flow tests	
HYDRATE: HIGH Ca						
1	[1] S	S	110	110	110	75
2	S	S	270	280	280	104
3	S	S	100	110	110	81
4	S	S	300	350	300	108
5	[2] U	U	80	120	120	85
6	U	S	120	120	120	73
7	S	S	240	250	240	91
8	S	S	180	140	140	96
9	S	S	100	120	120	86
10	S	S	420	440	330	100
11	U	U	150	140	120	89
12	S	S	130	140	160	99
13	U	S	180	210	180	96
14	S	S	120	120	120	79
15	S	S	70	70	----	----
16	S	S	50	120	----	----
17	S	S	80	80	----	----
HYDRATED: DOLOMITIC						
18	S	S	430	440	290	103
19	S	S	490	510	310	95
20	U	U	330	360	300	101
21	U	U	300	250	260	92
22	S	S	520	540	440	108
23	U	S	330	320	----	----
24	S	S	80	90	----	----
QUICKLIME: HIGH Ca						
25	U	U	>600	>600	220	108
26	S	S	350	360	230	114
27	U	U	160	180	130	101
28	S	S	>600	>600	430	111
29	S	S	>600	>600	>600	114
30	S	S	>600	>600	>600	113
31	S	S	>600	>600	>600	117
32	S	S	>600	>600	>600	115
33	S	S	180	180	150	111
34	S	S	>600	>600	>600	113
35	U	S	130	150	----	----
36	S	S	>600	>600	----	----
37	S	S	>600	>600	----	----
38	----	----	250	250	----	----
39	S	S	550	540	----	----
QUICKLIME: DOLOMITIC						
40	U	S	160	180	150	94
41	U	S	360	340	----	----
42	U	S	100	60	----	----
43	U	U	350	350	----	----

[1] S=Sound.
[2] U=Unsound.

(b) PLASTICITY

Portland cement mortars, in general, have the disadvantage as masonry materials of being harsh to work. Lime is often added with the idea of improving the plasticity and water-retaining power of the mortar mix, considerable attention generally being paid to the proportions of the mix and little or none to the plasticity or water-retaining power of the lime. Accordingly, plasticity determinations were made of stiff lime putties prepared from the hydrated limes and pulverized quicklimes by the method previously described, using the Emley plasticimeter, the instrument accepted by the lime industry for ascertaining the plasticity of lime.[4]

The Emley plasticimeter measures the torque of a steel disk against a revolving pat of lime putty as the putty stiffens on a standardized porous base-plate. It can be seen from the equation used to evaluate the plasticity, namely $P=\sqrt{F^2+(10t)^2}$, where P is the plasticity, F the torque reading, and t the time in minutes, that the longer the putty remains on the base-plate without stiffening the greater the plasticity. Thus, the plasticimeter indirectly gives information relative to the water-retaining properties of a lime putty and its troweling qualities, factors which are of concern to both plasterers and masons.

At the time the tests were made the putties were brought to standard consistency by the gradual addition of water accompanied by vigorous stirring—thus assuring a maximum plasticity of the putty, a procedure necessary to obtain consistent results.

The plasticity values, shown in table 1 and obtained with putties soaked for 1 day and 3 days before testing, varied from 50 to more than 600. The highest values were obtained with putties prepared from pulverized quicklimes and the lowest with those from hydrated limes.

How much greater than 600 the plasticity values of some of the very plastic quicklime putties were could not be determined definitely for the following reasons. In general the very plastic putties when brought to standard consistency contain more water than do nonplastic putties (plasticity less than 200). Even though they give up their water less readily to the porcelain base-plate of the plasticimeter than do the nonplastic putties, sufficient water has entered the base-plate at the end of an hour so that further stiffening of the putties takes place at a still further reduced rate. Because the absorption capacity of the base-plate is limited the instrument is not particularly suited to distinguish differences in very high plasticity values. Consequently, it seemed best to indicate merely that the plasticity values of such putties were greater than 600 rather than to ascribe exact values.

For very plastic limes it has been shown that the determination of the time of decided stiffening of the putty is largely the determining factor in the ultimate plasticity value. For nonplastic limes, where t is small, the value of F in the equation for calculating plasticity becomes of increasing importance. Since nonplastic lime putties, in general, give high F values, the plasticity value P is raised relatively more than that of the plastic putties. Nevertheless, many lime putties, especially those prepared from hydrated limes, have plasticity

[4] Federal Specification SS-L-351 for Lime; Hydrated (for) Structural Purposes. Also Tentative Methods for Physical Test for Limestone, Quicklime, and Hydrated Lime, ASTM designation: C 110-34T, Proc. Thirty-Seventh Annual Meeting, Am. Soc. Testing Materials 34, I, 754 (1934).

values below 200 (the arbitrary minimum value for a plastic putty), and there are indications that their plasticity would be even less than that calculated were it not for the factor mentioned.

The above discussions have been given to point out the great differences in the plasticities of lime putties rather than to emphasize the difficulties in securing exact values of plasticity at the extremes. Even with these difficulties the instrument is useful for classifying lime putties as plastic or nonplastic. Exact plasticity values of lime putties over the entire range become of importance, however, when plasticity is considered as a function of some other property.

The performance of the plasticimeter, especially at the point of separation of the plastic from nonplastic putties (i. e., 200), is illustrated in figure 1. That the plasticity of mixtures of two lime putties is a

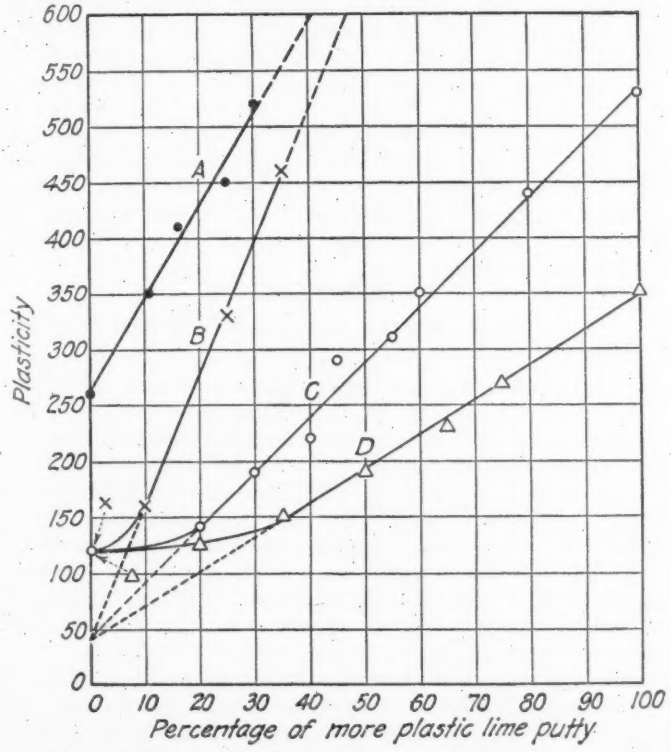

FIGURE 1.—*Effect on plasticity of adding a more plastic lime putty to one less plastic.*

straight-line function when the plasticity is greater than 150 is indicated in this figure wherein the plasticity is plotted against the percentage of the more plastic lime putty. Line *A* shows the increase in plasticity resulting from the addition of a very plastic putty to one having a plasticity of 260. *B*, *C*, and *D* show the increases when three plastic lime putties are mixed with a nonplastic putty. Above about 150 it can be seen that the plasticities of the mixtures of the three plastic limes with the nonplastic lime appear to be three straight lines which upon extrapolation downward indicate that the nonplastic lime putty should have a plasticity value of 40. The value obtained with the plasticimeter, however, was 120. On the other hand, lines *A* and

B, if extrapolated upward, would indicate that the plasticities of the two very plastic limes used in preparation of these two series of mixtures were far in excess of 600, being roughly twice that value.

It is often believed that the plasticity of lime putties always increases as the time of soaking is increased. Table 1 shows that in a few cases the plasticity increased with soaking from 1 to 3 days, in others there was no improvement, and some showed an actual decrease in plasticity. Consequently, the plasticity was determined also 3 to 4 weeks later at the time the flow tests were made on lime-sand mortars. These values, given under the column heading "plasticity at time of flow tests", show that in many instances the plasticity of the putties had decreased considerably.

As mentioned previously, lime putties stiffen as water is removed by the porous base-plate of the plasticimeter. A neat portland cement paste when tested with the plasticimeter will stiffen not only for the same reason but also because of the hydraulic properties of the cement. Therefore, the instrument is not particularly suited for measuring the plasticity of cements. Nevertheless, the two cements used in this study were mixed separately with sufficient water to bring the neat paste to the standard consistency used in testing limes and the plasticity was determined the same as with lime putties. The plasticity value obtained for each of the two cements was 120, and although low it is higher than the values obtained for some of the nonplastic hydrated limes.

2. MORTARS

(a) PROPORTIONING, MIXING, AND TESTING

Although the Emley plasticimeter indicates that there is a great difference in the plasticity and water-retaining capacity of lime putties, it is not well adapted to indicate these differences when the putties are incorporated with sand and other materials as mortars. Consequently, the water-retaining capacity of the mortars was determined with the apparatus developed by J. S. Rogers and R. L. Blaine [5] and described by L. A. Palmer and D. A. Parsons,[6] consisting essentially of a perforated dish resting on a funnel connected to a mercury-column relief valve and to a water aspirator. This apparatus can be used to determine the rate of removal of water from mortars. If the resulting change in flow of the mortar is also determined, the rate of stiffening of mortars on a porous base can be determined.

In general, the mortars were proportioned so that there was one volume of cementitious material to about three volumes of loose sand. Actually, proportioning was done by weight, assuming that portland cement weighs 94 lb/ft^3, dry hydrated lime, 40 lb/ft^3, and that 1 ft^3 of loose damp sand contains 80 lb of dry sand. For the sake of brevity, cement is indicated by the latter *C*, lime by *L*, and sand by *S*. In preparing the lime-sand mortars, lime putty, containing the equivalent of 100 g of dry hydrate, and 600 g of dry sand were mixed with a spatula, adding water gradually and stirring vigorously (to develop maximum plasticity) until the desired consistency had been attained. The flow was then determined by measuring the percentage increase in diameter of a mass of mortar on a standard 10-in flow table,[7] dropping the table top through a height of 0.5 in 25 times in 15 seconds. The mortar mix was finally adjusted with water until several determina-

[5] *Investigation of commercial masonry cements*, J. Research NBS **13**, 811–849 (1934) RP746.
[6] *Rate of stiffening of mortars on a porous base*, Rock Products **35**, No. 18, 18–24 (1932).
[7] Federal Specification Hydraulic Cements: Methods of Sampling, Inspection and Testing, SS-C-158 (September 30, 1936).

tions showed an average flow of 130, individual variations being 10 or less. The cement-lime-sand mortars were also stirred vigorously and adjusted to a flow of 130 percent. Vigorous stirring of cement-sand mortars was not as essential as in the case of mortars containing lime.

The mortars thus prepared were placed in the cup of the filtration device, spread gently to avoid compacting, and leveled even with the rim. A suction equivalent to a head of 2 in. of mercury was then applied. Immediately after the suction period the mortar was transferred back to the flow table cone and the "flow after suction" determined.

A few experiments were also made to observe how much the flow of lime-sand mortars was decreased when spread on sand-lime bricks in the approximate thickness of a mortar joint. The mortars were first brought to a flow of 130 percent and then placed in a metal form

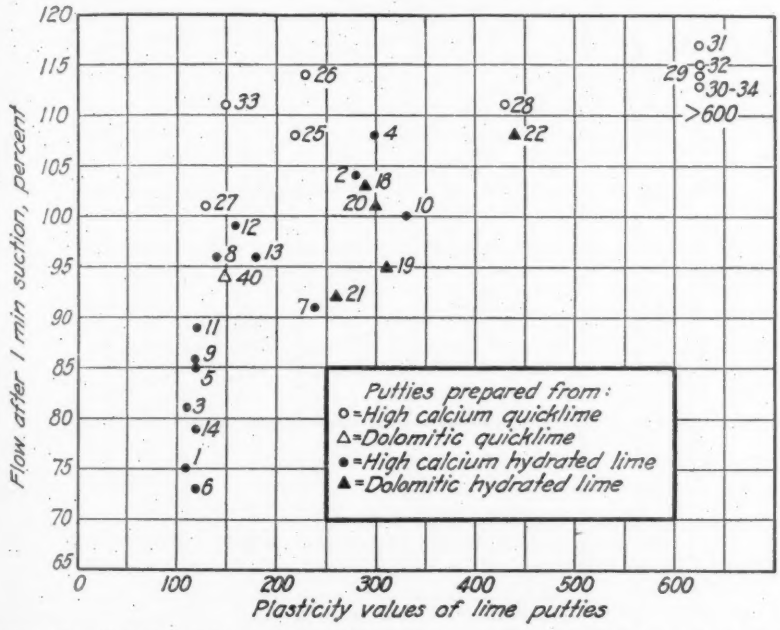

FIGURE 2.—*Relation between flow of lime-sand mortars (adjusted to a flow of 130 percent) after 1 minute of suction and plasticity of lime putties.*

(8 in. by 3¾ in. by ⅝ in.) resting on a flat side of the brick. The mortar was "struck off" and after 10 minutes the form was lifted and the mortar scraped from the brick into the cone of the flow table and the flow again determined. The bricks used in the tests had an average 5-hour cold absorption of 9.1 ±0.1 percent, by weight.

(b) RELATION BETWEEN PLASTICITY OF LIME PUTTIES AND FLOW AFTER SUCTION OF LIME-SAND MORTARS

Figure 2 shows the flows resulting after 1 minute of suction of lime-sand mortars (initial flow of 130) plotted against the plasticity of the lime putties used in preparing the mortars. The figure shows that there is a large spread in the flows after suction (73 to 117 percent) and that none of the more plastic limes gave the lower values for the flow

after suction. In general, mortars containing putties prepared from the pulverized quicklimes gave higher flows after suction than did those containing putties prepared from the hydrated limes. All of the lime putties having plasticity values between 110 and 120 formed mortars having flows after suction of less than 90 percent. It is these nonplastic putties which appear to have even lower extrapolated plasticity values than those indicated by the Emley plasticimeter (see fig. 1). Had these lower extrapolated values in plasticity (40 to 50 instead of 110 to 120) been plotted in figure 2 against the flow after suction, it would have been more evident that the flow after suction of a lime-sand mortar is dependent on the plasticity of the putty used in pre-

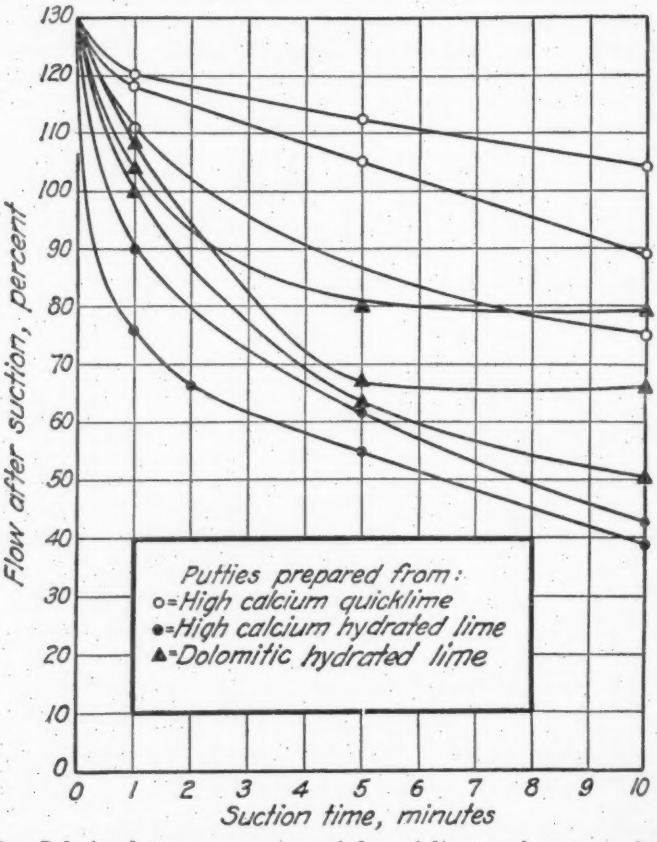

FIGURE 3.—*Relation between percentage of flow of lime-sand mortars after suction and time of suction in minutes.*

paring the mortar. Figure 2 shows also that the use of putties having high plasticity values will insure mortars of high flow after suction.

The rates of stiffening of eight lime-sand mortars are indicated in figure 3 by the percentage of flow at increasing time of suction. The eight lime putties used in preparing the mortars were chosen because they gave a wide range in plasticity values and flow after 1 minute of suction. The results confirm, in general, those obtained by Palmer and Parsons [8] in that the mortars made from putties prepared from

[8] *Rate of stiffening of Mortars on a porous base*, Rock Products **35**, no. 18, 18–24 (1932).

quicklimes do not decrease in flow as rapidly as those prepared from hydrated limes.

Figure 4 shows the flows resulting after 10 minutes, suction of lime-sand mortars plotted against the plasticity of the lime putties at the

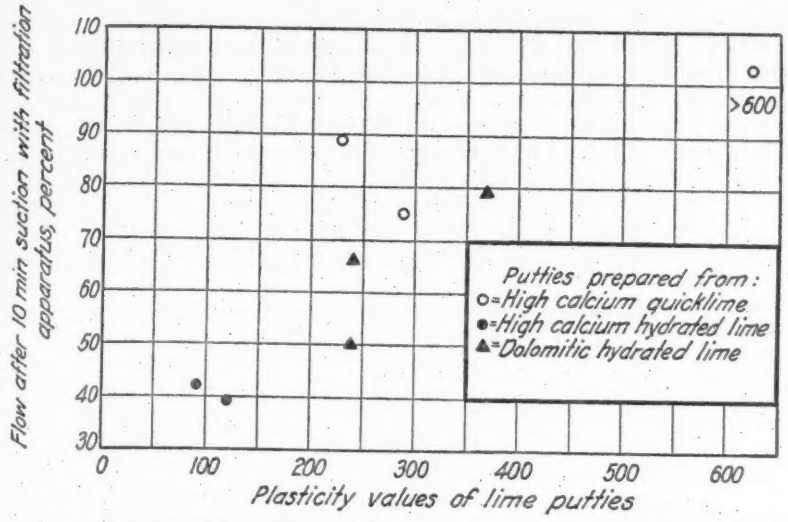

FIGURE 4.—*Relation of flow of lime-sand mortars after 10 minutes' suction to plasticity of the lime putty used in preparing the mortars to an initial flow of 130 percent.*

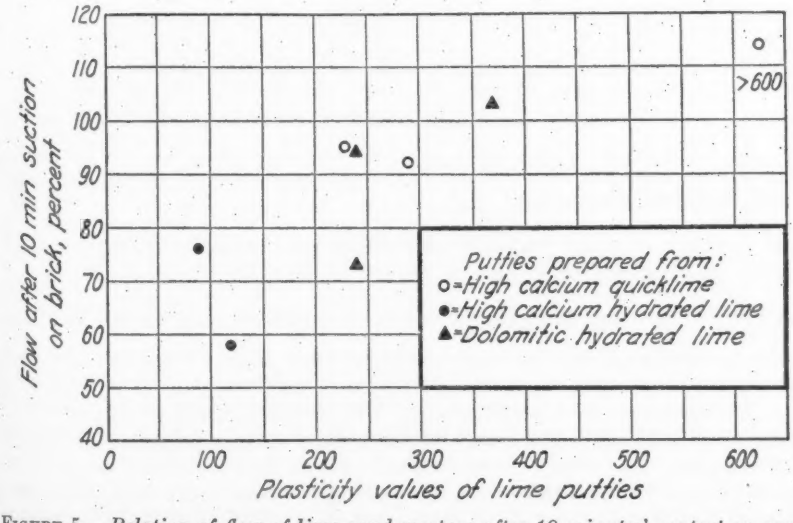

FIGURE 5.—*Relation of flow of lime-sand mortars after 10 minutes' contact on sand-lime brick to plasticity of the lime putty used in preparing the mortars to an initial flow of 130 percent.*

time they were used in preparing the mortars. This plot shows, as illustrated by figure 2, that the flow after suction of a lime-sand mortar in general increases as the plasticity of the limes used in preparing the mortars increases.

These same lime-sand mortars were used also to determine how much the flow was decreased when they were spread on bricks in the approximate thickness of a mortar joint according to the procedure previously outlined. Figure 5 shows the flows of the mortars at the end of 10 minutes' contact with the brick plotted as a function of the plasticity of the constituent lime putties. As shown also with the filtration apparatus, the flow of lime-sand mortars resulting from contact with porous bodies is dependent largely upon the plasticity of the lime putty used.

Since the flow of lime-sand mortars determined both after a ten minute suction period with filtration device and on bricks were related to the plasticity of the lime putties, it is evident that the filtration device can be used to indicate the behavior of a mortar in contact with a sand-lime brick. This relation is illustrated in figure 6. These relations were obtained with but one make of sand-lime brick

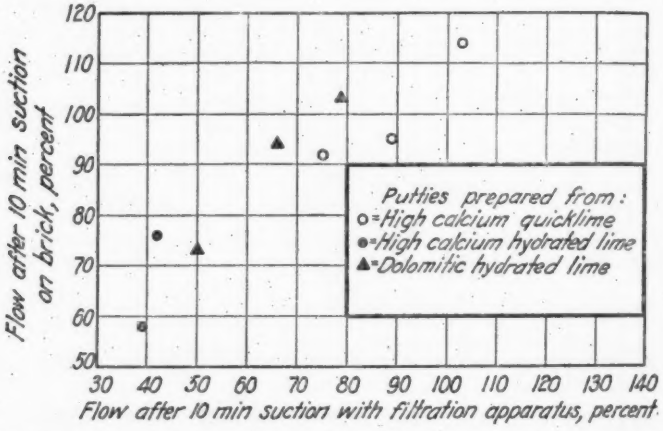

FIGURE 6.—*Relation of flow (in percent) of lime-sand mortars after 10 minutes' suction on sand-lime brick to flow (in percent) obtained after 10 minutes' suction with the filtration apparatus.*

and further studies on different types of brick representing wide ranges in absorptive properties would be of interest.

(c) EFFECT OF DIFFERENT LIMES ON FLOW OF CEMENT-LIME-SAND MORTARS

Since the studies on lime-sand mortars indicated that the flow after suction of the mortars decreased in general as the plasticity of the lime putties used in preparing the mortars decreased, three lime putties of high, intermediate, and low plasticity values, respectively, were chosen to study their effects on cement-lime-sand mortars. Lime *A* was a putty prepared from a high-calcium quicklime having a plasticity value greater than 600; lime *B* a putty from a high-calcium hydrated lime with a plasticity value of 280; and lime *C* a nonplastic high-calcium hydrated lime putty with a plasticity value of 120.

Figure 7 shows the change in flow after suction resulting from the addition of increasing amounts of the three limes to portland cement *A*. The proportions of the constituents of the mortar are indicated both on a weight and volume basis. A factor worthy of note is that the kind of lime used and manner of using are of more importance in

securing a high flow after suction than is the proportioning. Thus, the relatively small quantity of lime putty A in the mortar $1C$:$0.25L$:$3S$ by volume increased the flow after suction of a straight cement-sand mortar ($1C$:$3S$ by vol.) from 46 to 87, a value greater than that of the straight lime-sand mortar prepared from putty C. When lime C was not soaked to make a putty but was added as the dry hydrate to the mortar it gave a still lower value. Also, when added in this way in preparing a cement-lime-sand mortar (a common practice), lime C increased the flow after suction but slightly. The increase in flows between a $1C$:$1L$:$6S$ by volume and a $1C$:$2L$:$9S$ by volume resulting from an increase in the proportions of both lime C (not soaked) and lime A are negligible as compared to the difference

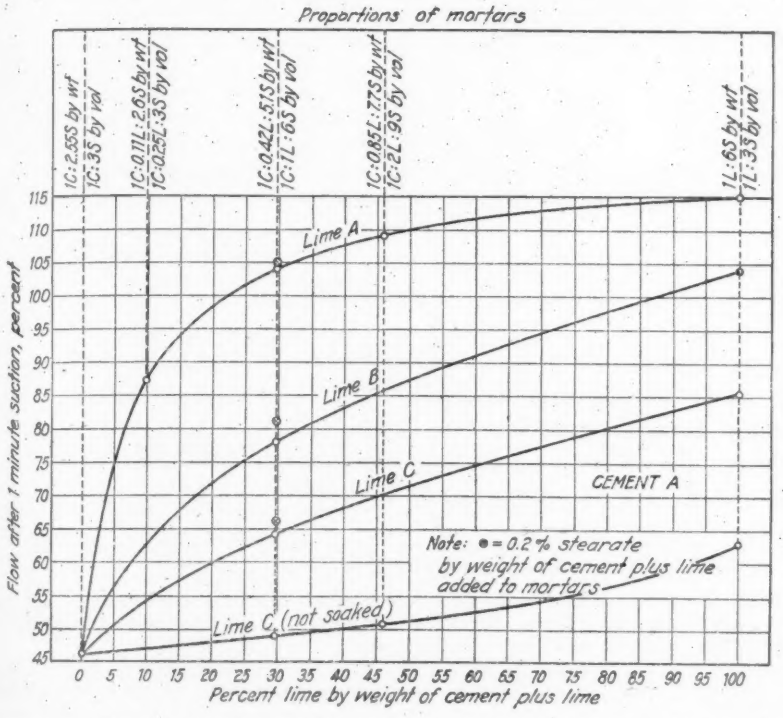

FIGURE 7.—*Relation between the flow after 1 minute suction of mortars resulting from the substitution of different limes for a typical portland cement and the percentage of limes substituted for the cement.*

Specific surface of cement A was 1,750 cm²/g and plasticities of lime putties A, B, and C were greater than 600, 280, and 120, respectively. Prior to suction all mortars were brought to a flow of 130 percent.

obtained with the use of lime A in preference to lime C (either soaked or not soaked).

Figure 7 shows also that the addition of 0.2 percent of stearate increased but little the flow after suction of the mortars $1C$:$1L$:$6S$ by volume using putties A, B, and C.

The flows after suction of mortars made by adding putties A, B, and C to a cement-sand mortar made with the cement B, are shown in figure 8. Comparison of figure 8 with figure 7 shows that with the use of a cement of high specific surface (cement B), the flow after

suction of a cement-sand mortar increases over that obtained by use of a typical portland cement (cement A). This increase, however, is small in comparison with that obtained with a lime putty similar to lime A. The addition of only 0.25 parts by volume (0.11 by weight) of this lime increased the flow after suction of the typical portland cement-sand mortar more than twice that attained when the high-early-strength cement B was substituted for cement A in the $1C{:}3S$ mortar. The flow after suction of mix $1C{:}1L{:}6S$ by volume was practically the same (105 ± 1) when both of these cements were used with lime A. Figure 8 shows also that the flow after 1-minute suction of the cement-sand mixture $1C{:}3S$ by volume was practically the

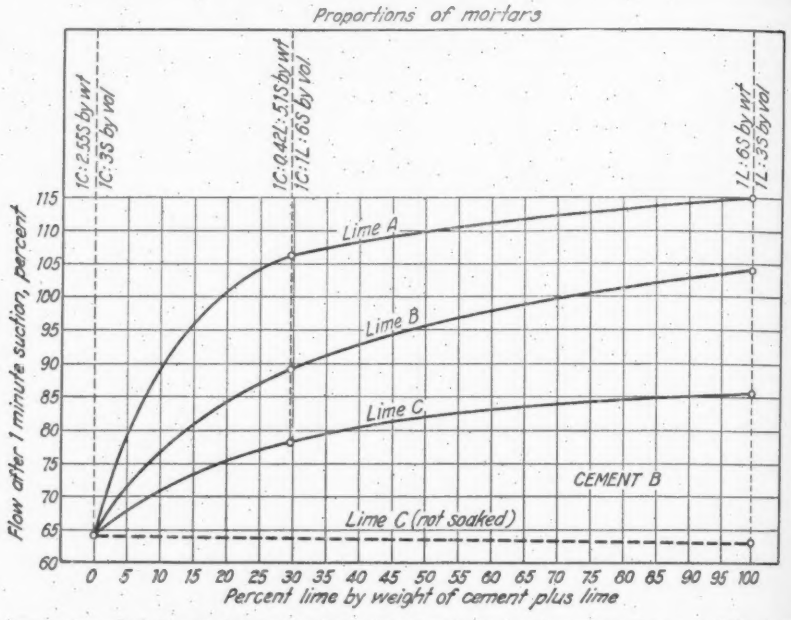

FIGURE. 8.—*Relation between the flow after 1 minute suction of mortars resulting from the substitution of different limes for a cement of high specific surface and the percentage of limes substituted for the cement.*

Specific surface of cement B (high-early-strength) was 2,750 cm²/g and plasticities of lime putties A, B, and C were greater than 600, 280, and 120, respectively. Prior to suction all mortars were brought to a flow of 130 percent.

same as that obtained with the straight lime-sand mortar prepared with the unsoaked lime C.

IV. SUMMARY

A survey was made of the soundness and plasticity of lime putties made from 43 commercial limes, including pulverized quicklimes and hydrated limes. Lime putties were used also in preparing lime and cement-lime mortars adjusted to a flow of 130 percent. Part of the water was then removed by a suction device and by contact with sand-lime brick and the resulting "flows after suction" were determined.

When the 43 lime putties were soaked 1 day prior to testing (by steaming lime-gypsum pats at 120 lb./in.² for 2 hours), 7 of the 24 hydrated limes and 8 of the 19 quicklimes were classified as unsound.

After soaking 3 days, four of the hydrated lime putties, and four of the quicklime putties were unsound.

The plasticity values of the 43 lime putties prepared by soaking limes for 1 day ranged from 50 to more than 600, the most plastic putties being those prepared from quicklimes.

Nineteen of the putties had higher plasticities after 3 days of soaking than they did after 1 day of soaking, but six of them were less plastic.

The flows of lime mortars after 1 minute of suction varied from 73 to 117 percent.

In general, lime mortars prepared from quicklime putties gave higher flow values after suction than they did when prepared with hydrated limes.

Flow after suction of lime mortars (whether determined with a suction apparatus or with mortars which had been placed on sand-lime brick) is dependent on the plasticity of the putty used in preparing the mortar.

Addition of a nonplastic dry hydrated lime increased the flow after suction of a portland cement mortar but little. Using the same lime as an aged putty gave higher flows after suction.

The flow after suction of cement-lime mortars depends far more on the properties of the lime than on the cement-lime ratio.

WASHINGTON, September 29, 1936.

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RESEARCH PAPER RP953

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EXTRACTION, WITH ACETONE, OF SUBSTANTIALLY CONSTANT-BOILING FRACTIONS OF A "WATER-WHITE" LUBRICATING OIL[1]

By Beveridge J. Mair and Sylvester T. Schicktanz[2]

ABSTRACT

This paper describes the separation, with respect to type of molecule, effected by solvent extraction of substantially constant-boiling fractions of a "water-white" lubricating oil. Each charge of about 500 g was separated, by extraction in 14-m columns, into from 25 to 35 fractions. Kinematic viscosities at 100 and 210° F and refractive indices were determined on all fractions. In addition to the properties mentioned, carbon-hydrogen ratios, molecular weights, densities, dispersions, optical activities, boiling points, and aniline points were determined on about 30 "key" fractions. The extractor columns and their mode of operation are described.

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I. INTRODUCTION

This paper presents a continuation of the work on the chemical constitution of lubricating oil, undertaken at the National Bureau of Standards as part of the American Petroleum Institute Research Project 6. In particular, it describes the separation, with respect to type of molecules, effected by solvent extraction of oil which had previously been extensively distilled and which was substantially constant boiling. A correlation of the physical properties of certain fractions from this extraction process and their comparison with those of synthetic hydrocarbons of high molecular weight follows in a subsequent paper.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum. This paper was originally presented before the American Chemical Society at the Pittsburgh meeting in September 1936.

[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

II. PRELIMINARY TREATMENT OF THE LUBRICANT FRACTION AND SCOPE OF THE PRESENT WORK

The preliminary treatment of the lubricant fraction of the mid-continent petroleum used in this work has been described previously [1] [3] and is illustrated graphically in figure 1. It consisted in separating the lubricant fraction by successive treatments into three parts: (1) An extract portion by extraction with sulphur dioxide; (2) a wax portion by crystallization from ethylene chloride at −18° C; and (3) a "water-white" oil portion by filtration through silica gel. This paper deals with the water-white portion only, the investigation of which was begun by distilling it under high vacuum with the object of separating it into fractions differing in molecular weight. The light and heavy ends from this distillation were placed in storage as indicated in figure 1, and distillation of the remainder was continued until substantially constant-boiling fractions were obtained. Charges were prepared for extraction by mixing according to their viscosities, the distillation fractions of about 45 g each. The weight of these charges and the approximate range in kinematic viscosity at 100° F and refractive index at 25° C of the fractions which it was necessary to mix to prepare each charge are shown in figure 1 under *Charges for Extraction*. Each charge was separated into from 25 to 35 fractions by extraction with acetone in 14-m columns. Kinematic viscosities at 100 and 210° F and refractive indices at 25° C were determined on all fractions from the extractors. However, these properties are reported only for the series designated in figure 1 as *A*, *B*, *C*, *D*, *E* and *F*, which were regarded as typical. In addition for the same series, carbon-hydrogen ratios, molecular weights, densities, dispersions, optical activities, boiling points, and aniline points were determined on certain "key" fractions.

III. DISTILLATION

The systematic distillation under high vacuum of the water-white oil was continued, using the equipment and procedure described previously [1]. When the range in viscosities of the fractions resulting from the distillation of each charge, particularly for the more volatile portions, finally became nearly as small as the range in viscosity of the fractions which were blended to make up a charge, it was decided that it was unprofitable to continue the distillation further. In figure 2 are plotted the viscosities of fractions resulting from the final distillation with respect to the percentage by weight of the charge. Curves for all the charges are not included, but those given are typical. On the right-hand side of the figure are indicated the weights of the individual charges, together with the range in viscosities of the fractions which it was necessary to mix to prepare a charge. Curves *I* to *V* are the result of seven distillations in short fractionating columns, while curves *VII* to *X* represent the result of four distillations in a column molecular still, followed by from four to seven distillations in simple molecular stills. Curve *VI* is the result of eight stages of molecular distillation followed by one distillation in a short fractionating column. There was of course an interchange between the two types of distillation, the more volatile

[3] The figures given in brackets here and elsewhere in the text correspond to the numbered references at the end of this paper.

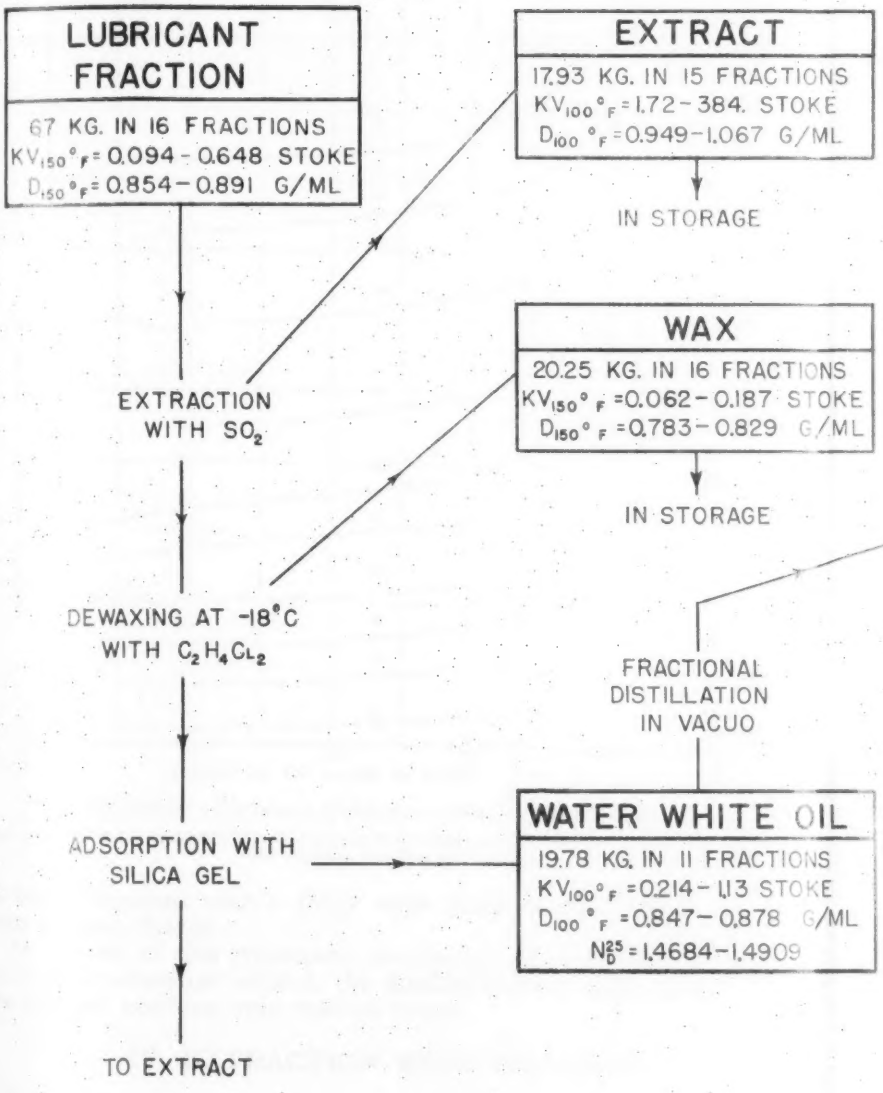
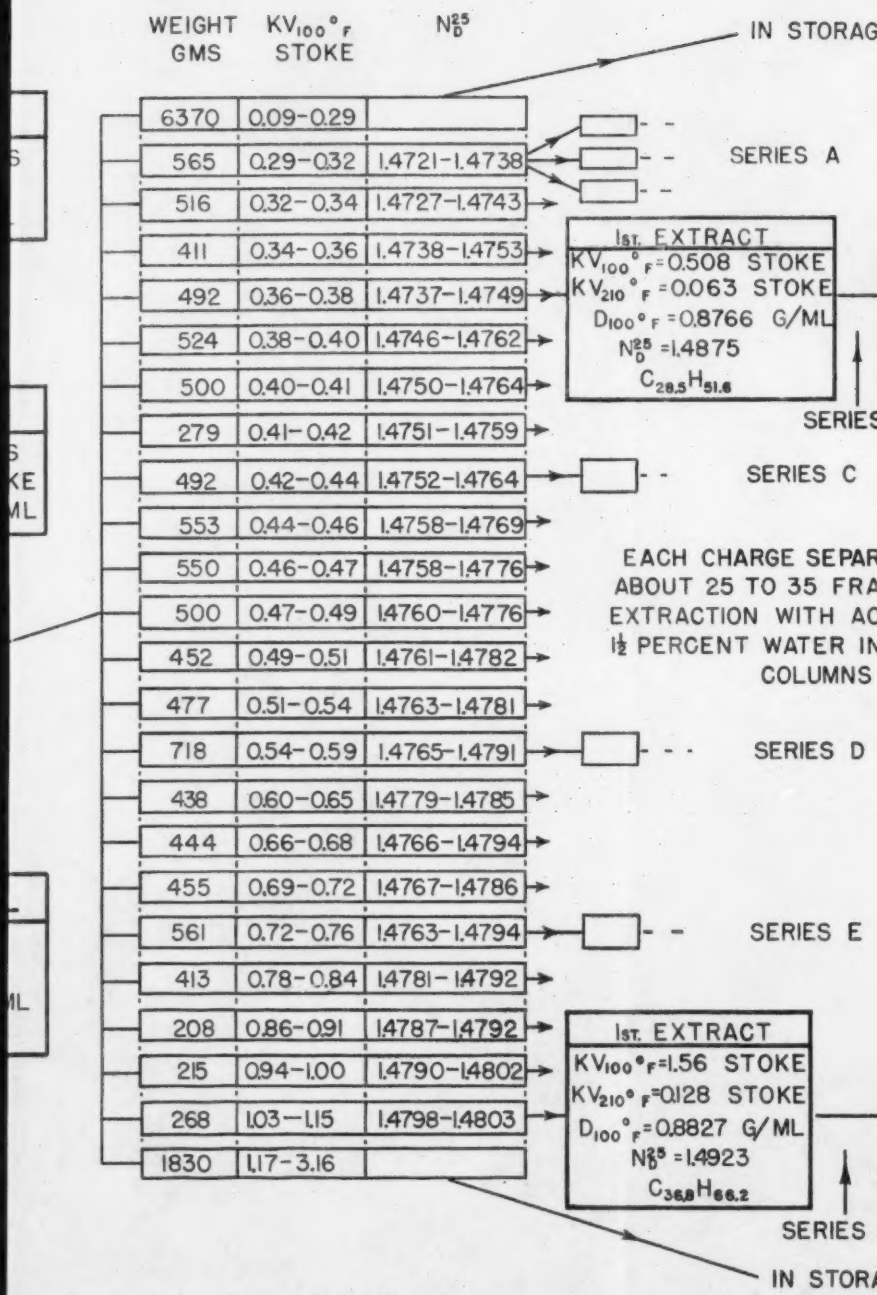

FRACTIONS FROM
PRELIMINARY SEPARATIONS
LUBRICANT FRACTION
67 KG. IN 16 FRACTIONS
KV150°F = 0.094 - 0.648 STOKE
D150°F = 0.854 - 0.891 G/ML
EXTRACT
17.93 KG. IN 15 FRACTIONS
KV100°F = 1.72 - 384. STOKE
D100°F = 0.949 - 1.067 G/ML
IN STORAGE
WAX
20.25 KG. IN 16 FRACTIONS
KV150°F = 0.062 - 0.187 STOKE
D150°F = 0.783 - 0.829 G/ML
IN STORAGE
EXTRACTION WITH SO2
DEWAXING AT -18°C WITH C2H4Cl2
FRACTIONAL DISTILLATION IN VACUO
WATER WHITE OIL
19.78 KG. IN 11 FRACTIONS
KV100°F = 0.214 - 1.13 STOKE
D100°F = 0.847 - 0.878 G/ML
ND25 = 1.4684 - 1.4909
ADSORPTION WITH SILICA GEL
TO EXTRACT

FIGURE 1.— *Chart showing treatment and*

TIONS

CHARGES FOR EXTRACTION

FRACTIONS EXTRACT



treatment and disposition of lubricating oil fractions.

ONS FROM
RACTION

STORAGE

S A

RAFFINATE
KV_{100} °F 0.230 STOKE
KV_{210} °F=0.045 STOKE
D_{100} °F=0.8274 G/ML
N_D^{25} =1.4625
$C_{29.0}H_{57.7}$

SERIES B

IES C

SEPARATED INTO
35 FRACTIONS BY
ITH ACETONE PLUS
ATER IN 14 METER
LUMNS

RIES D

RIES E

RAFFINATE
KV_{100} °F=0.733 STOKE
KV_{210} °F=0.095 STOKE
D_{100} °F=0.8470 G/ML
N_D^{25} =1.4714
$C_{38.4}H_{74.7}$

SERIES F

N STORAGE

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fractions from the molecular stills (below 0.60 stoke) being charged for the next distillation into the fractionating columns, while the less volatile fractions from the fractionating columns (above 0.60 stoke) were charged into the molecular stills.

A greater range in the viscosity of the fractions from the distillation of the less volatile charges is noticeable. This may be due in part to the limited quantity of oil in this region, it being necessary

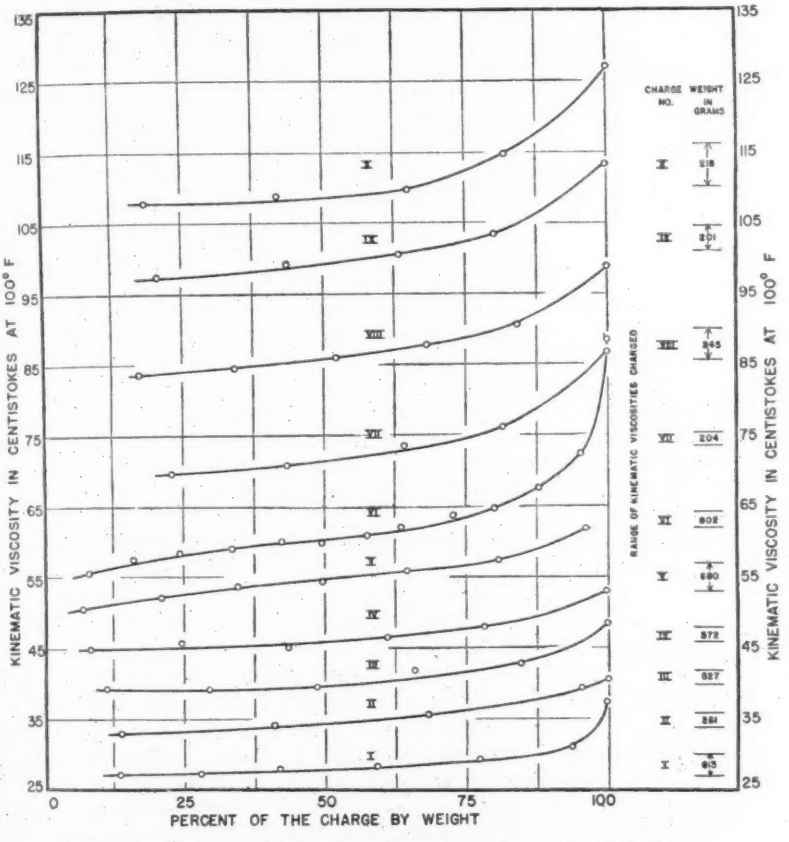

FIGURE 2.—*Viscosities of fractions from the final distillation.*

Each point represents by its ordinate the viscosity of a fraction, by its abscissa the percentage which had been distilled, including the fraction.

to blend fractions with a fairly wide range in viscosity to prepare even a small charge.

At the end of this systematic distillation, the oil originally water-white was somewhat colored, the distillates being pale yellow, while the still-pot residues were reddish brown.

IV. EXTRACTION WITH SOLVENTS

A powerful tool for investigating the composition of lubricating-oil fractions is now available in extraction with solvents. Solvents have been used for many years to effect a separation of the various

types of hydrocarbons in petroleum. It is only recently, however, that the twofold action of solvents in separating both with respect to molecular weight and with respect to type has been clearly recognized. It is evidently of importance to extract fractions composed of hydrocarbons with a narrow range of molecular weights if the maximum separation with respect to type is to be obtained. Consequently, the extraction experiments of the earlier investigators were not particularly successful, since they used fractions of wide boiling range and obtained fractionation with respect to both type and molecular weight.

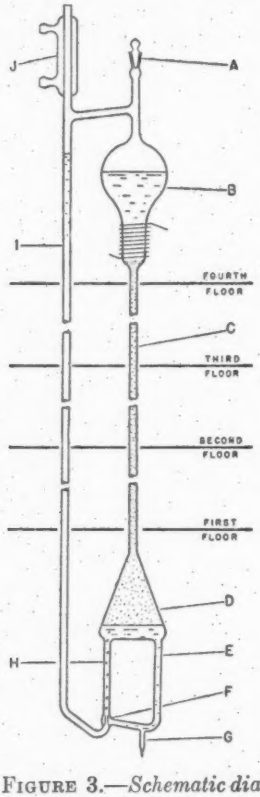

FIGURE 3.—*Schematic diagram of extractor.*

Recently, also, Saal and Van Dyck [2], by drawing attention to the analogies between distillation and solvent extraction and emphasizing the importance of reflux in extraction, have pointed the way to the more efficient use of solvents. Fenske and coworkers [3] have made notable contributions in this field and have constructed columns which utilize the idea of reflux and which give exceptionally good separations. We are indebted to Professor Fenske for communicating to us, prior to publication, descriptions of his extraction columns. Columns similar to Fenske's, designed for the small charges available, have been erected in this laboratory and have proved effective in separating the narrow distillation fractions with respect to type.

V. DESCRIPTION OF EXTRACTORS

In figure 3 is shown one of the extractors used with acetone, or acetone with 1.5 percent of water, as a solvent. It was constructed entirely of Pyrex glass. It consisted of the 500-ml kjeldahl flask, *B*, from which the solvent was distilled to the condenser, *J*, and from which it flowed through the tube, *I*, then through the oil in the erlenmeyer flask, *D*, (500 to 700 ml), returning again saturated with oil to the flask, *B*. When the solvent in flask *B* became saturated, oil came out of solution in the form of small globules, which, being heavier than the solvent, sank slowly to flask *D* against the ascending stream of solvent saturated with oil. The solvent entered the oil in the form of globules through the injector, *F*, and carried upward with it a stream of oil into flask *D*. This caused a circulation of oil through the system *H*, *D*, *E*, and insured thorough mixing of the oil and intimate contact with the solvent. The tubes *E* and *H* extended 30 cm below flask *D*. Distillation of the solvent was accomplished by electrical heating, the lower portion of the kjeldahl flask, *B*, being surrounded with an asbestos-insulated heating coil. To maintain smooth boiling the lower portion of the inside of flask *B* was coated with carborundum. *A* is a ground-glass joint, through which the

charge of oil and the solvent were introduced, and through which the individual fractions of acetone saturated with oil were withdrawn. *G* is a fine glass tip, which was broken when it was necessary to withdraw the oil residue and solvent left at the end of an experiment.

The desirability of obtaining a maximum separation of the comparatively small charges of oil (about 500 g) governed the choice of the dimensions of these extractor columns. It was important that the path where the counterflow of saturated acetone and oil globules occurred be as long as possible, and also that the "hold-up"; i. e., the amount of oil in solution and in the form of globules, in the column, represent a small fraction of the charge. For these reasons very tall extractor tubes with very small diameters were chosen. The extractors were located in an elevator shaft and extended from the basement to the fourth floor, a distance of about 14 m (C, fig. 3). Extractors with tubes 8, 6, and 4 mm in internal diameter were constructed. The 4-mm tubes, however, proved impractical since they clogged frequently with oil.

VI. CHOICE OF SOLVENT

Acetone, or acetone containing 1.5 percent of water, which was thought to be slightly more selective than pure acetone, was selected as a solvent. Many highly selective solvents—i. e., those solvents which give a good separation with respect to type—have been reported. Most of these, however, boil at elevated temperatures and were thought likely to be difficult to remove completely from the oil, and also likely to attack the oil at the temperatures necessary to distil and circulate them in the type of column just described. Methyl cyanide, one of the lower boiling solvents, was tried, but the globules of oil instead of falling freely stuck to the glass tubing, eventually clogging the column.

VII. OPERATION OF EXTRACTOR COLUMNS

After the circulation of acetone had commenced, about 6 hours were required before the acetone in flask *B* was saturated and oil globules appeared. Two more hours were required before these globules traveled 14 m to the flask at the bottom of the column. After a suitable interval of time (16 to 32 hours) necessary for the attainment of equilibrium had elapsed, a fraction of acetone saturated with oil was withdrawn, and fresh acetone was added through the top of the condenser. This procedure was continued until all but a small residue of oil had been removed as fractions in solution in acetone. The greater part of the acetone was distilled off from the oil fractions, while the last traces were removed by sweeping out with carbon dioxide for 12 hours at 100° C. The residue in the column, removed by breaking tip *G*, was freed from acetone in a similar manner. Fractions of about 15 g, the amount required for determining physical properties, were obtained. The size of these fractions depended on the solubility of oil in acetone, and could be controlled to some extent by varying the quantity of acetone (200 to 350 ml) in flask *B*. It can be seen that this mode of operating is analogous to fractional distillation under total reflux. The oil container, *D*, corresponds to

the still pot, the flask, *B*, to the reflux condenser and receiver, while the column itself is analogous to the column in fractional distillation. The oil in solution corresponds to the vapor phase in distillation while the oil globules correspond to the liquid reflux.

An enlargement of a photograph of a small section of an extractor column is shown in figure 4. The small size of the oil globules is apparent by comparing them with the scale on the left of the figure. They appear to vary from about 0.1 to 0.3 mm in diameter. Some magnification of the oil globules, along the horizontal axis, occurred in taking the photograph through glass and solvent. Small oil globules are desirable in obtaining a good separation, since the rapidity of attainment of equilibrium is dependent on the surface area.

The circulation of acetone in the extractors was maintained at a rate of about 1.5 ml per minute. If the rate was increased much beyond this value, the smaller globules began to rise and a clogging of the column resulted. The hold-up of the column—i. e., the amount of oil in solution and in the form of globules between flask *B* and oil container *D*—was determined for one of the 6-mm extractors by using a calibrated U-tube instead of the lower reservoir. The height of oil in this tube was noted when the circulation of solvent had first began and again over a period of hours until the level remained constant. From the difference in levels the volume of oil in solution and in the form of globules both in the column and in flask *B* was computed. The volume of oil in flask B was then determined and the difference gave the hold-up of the column. The hold-up, of course, depended on the fractions being investigated, the more soluble fractions giving the greater hold-up. For a distillation cut with kinematic viscosity at 100° F.=0.485 stoke, and using acetone containing 1.5 percent of water as solvent, the hold-up was 11.3 g for a 6-mm column operating at about 27° C. This hold-up would represent about 2 percent of a charge of 500 g.

VIII. DETERMINATION OF PHYSICAL CONSTANTS

Kinematic viscosities at 100 and 210° F. were determined with the aid of the assembly of viscosity pipettes previously described [1]. Where necessary, kinetic energy corrections were applied, and the results are believed accurate to within ±0.5 percent. Viscosity indices were computed with the aid of the tables given by Hersh, Fisher, and Fenske [4]. Density determinations were made with the aid of the same series of viscosity pipettes, each value recorded being the result of two determinations agreeing within 0.1 percent. Molecular weights were determined by the ebullioscopic method previously described [5], using benzene as a solvent. The results are considered accurate to within ±1 percent, although a precision as high as 0.2 percent was attained in any one determination.

Boiling points at 1 mm of Hg pressure were determined with the aid of a thermocouple calibrated by the Heat Division of this Bureau in an apparatus which has been described previously [6].

Aniline points were determined in the usual manner, with equal volumes of oil and freshly distilled aniline.

Dispersions were obtained from readings on the compensator drum of an Abbe refractometer and the tables provided with the instrument.

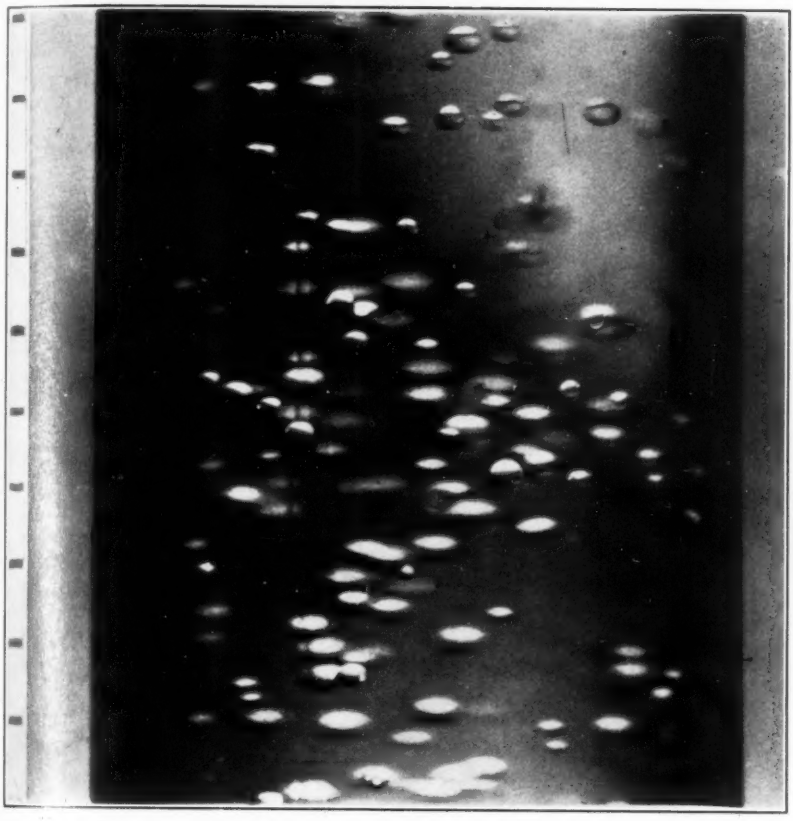

FIGURE 4.—*Small section of the reflux arm of the extractor, showing oil globules.*

The scale at the left is in millimeters.

The optical rotations were measured in a 2-dm tube with a saccharimeter in the Polarimetry Section of this Bureau and converted from °S to $[\alpha]_D$. A precision of about 0.01 in the values of $[\alpha]_D$ was obtained.

The iodine numbers were determined by the Detergents Section of this Bureau (Wijs method). In addition to the petroleum fractions the iodine number of the synthetic hydrocarbon, 1,1-tetralino-*n*-butyl-2-hexadecylethylene, was determined as a check on the accuracy of the iodine-number measurements. This hydrocarbon was kindly furnished by L. A. Mikeska of the Standard Oil Development Co. It should have an iodine number of 58, while the experimentally determined value was 67. Presumably the experimental results are somewhat high, indicating some substitution as well as addition.

IX. DETERMINATION OF CARBON-HYDROGEN RATIOS

The degree of accuracy attained in the combustion analyses is evidenced by the data in table 1 on the combustion of a sample of

TABLE 1.—*Combustion analyses of n-nonacosane* [1]

Weight of sample	Combustion analyses	
	Ratio: $\frac{\text{moles } H_2O}{\text{moles } CO_2}$	Mass sample less mass C+H
g		g/g
0.5215	1.0343	0.0012
0.5074	1.0345	.0008
0.5157	1.0342	.0009
Theoretical ratio	1.0345	

[1] These determinations were made by C. B. Willingham.

n-nonacosane.[4] This high accuracy was made possible by the use of (a) oxygen freed from carbon dioxide, water, hydrogen, and organic impurities in a purification train; (b) a quartz combustion tube containing platinized quartz and copper oxide; (c) the use of hydrogen, in the U-tube adsorbers, as described by Rossini [7], when weighing to minimize errors caused by changes in room temperature and in barometric pressure and to make more certain the change in volume of the solid adsorbents; (d) sealed connections, except for a ground-glass to quartz joint at the inlet end of the combustion tube, and ground-glass joints to attach the U-tube adsorbers to the combustion tube; and (e) a condensation chamber as used by Rossini [8] between the combustion tube and the U-tube adsorbers. This chamber collected temporarily the water and prevented it from condensing on the lubricated ground joints. From this chamber the water was slowly aspirated to the absorber. It was found important to prevent the sample from catching on fire in the platinum boat which contained it, since, when it caught on fire, there was a temporary depletion of the oxygen supply and incomplete combustion resulted, as evidenced by the deposition of carbon at the exit end of the combustion tube. Consequently, the greater part of the sample was aspirated through

[4] This sample was furnished by K. S. Markley, Bureau of Plant Industry, U. S. Department of Agriculture, who prepared it from apple cuticle.

the tube by slowly moving the small section of the furnace, by means of a thumbscrew, towards and over the sample. Only at the end of the experiment, when burning off carbon, was any flame visible in the boat. The atomic weights used in the computations were 12.009 for carbon and 1.0081 for hydrogen.

X. TABULATION OF RESULTS

Table 2 contains a tabulation of the kinematic viscosities at 100° and 210° F, viscosity indices, and refractive indices for all the fractions from series *A*, *B*, *C*, *D*, *E*, and *F* (see fig. 1), while table 3 records a more complete set of physical properties, together with their empirical formulas, of certain "key" fractions from the same series.

The fact that series *A* is listed in the tables as A_1, A_2, and A_3 requires some explanation. As shown in figure 1, the original charge from which this series was composed was divided into three parts, each of which was extracted separately. By blending the fractions from the three charges according to their physical properties three new charges were prepared, each of which was in turn extracted. It is the fractions from these second charges which are listed in tables 2 and 3 as series A_1, A_2, and A_3.

TABLE 2.—*Physical properties of petroleum fractions*

TABLE 2.—*Physical properties of petroleum fractions*

SERIES A_1

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at—		Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at—	
			100° F	210° F				100° F	210° F
%			*Stoke*	*Stoke*	%			*Stoke*	*Stoke*
0.0 to 11.2	1.5032	36	0.6259	0.0655	48.8 to 61.6	1.4836	39	0.6854	0.0695
11.2 to 20.2	1.5025	46	.5441	.0618					
20.2 to 34.7	1.4962	56	.5785	.0656	61.6 to 76.6	1.4778	64	.4887	.0606
34.7 to 48.8	1.4913	35	.7400	.0717	76.6 to 100	1.4701	98	.3078	.0497

SERIES A_2

0 to 5.4	1.4836	49	0.5987	0.0658	37.7 to 47.1	1.4717	93	0.3281	0.0511
5.4 to 9.7	1.4780		.4516		47.1 to 55.5	1.4709	97	.3163	.0504
9.7 to 15.1	1.4781	60	.4538	.0574	55.5 to 63.2	1.4706	97	.3114	.0499
15.1 to 21.1	1.4770	69	.4395	.0576	63.2 to 71.4	1.4704	92	.3016	.0483
21.1 to 28.9	1.4761	74	.4208	.0567					
					71.4 to 83.3	1.4664	110	.2638	.0464
28.9 to 37.7	1.4729	90	.3483	.0526	83.3 to 100	1.4647	123	.2306	.0438

SERIES A_3

0 to 6.5	1.4681	117	0.2457	0.0450	50.2 to 59.3	1.4609	136	0.2010	0.0414
6.5 to 11.8	1.4650				59.3 to 67.2	1.4612	134	.2027	.0414
11.8 to 30.3	1.4660	116	.2462	.0450	67.2 to 75.2	1.4607	137	.1977	.0410
30.3 to 41.5	1.4640	125	.2246	.0433	75.2 to 83.2	1.4604	141	.1908	.0404
41.5 to 50.2	1.4613	135	.2020	.0414	83.2 to 100	1.4587	149	.1808	.0398

TABLE 2.—*Physical properties of petroleum fractions*—Continued

SERIES *B*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at—		Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at—	
			100° F	210° F				100° F	210° F
%			*Stoke*	*Stoke*	%			*Stoke*	*Stoke*
0 to 6.6	1.4875	70	0.5084	0.0630	59.5 to 61.5	1.4728	95	0.3714	0.0556
6.6 to 12.5	1.4874	72	.4918	.0622	61.5 to 63.5	1.4730	93	.3780	.0559
12.5 to 18.4	1.4830	75	.4784	.0615					
18.4 to 23.2	1.4805	78	.4560	.0603	63.5 to 65.5	1.4721	96	.3612	.0548
23.2 to 25.9	1.4825	73	.4887	.0620	65.5 to 67.8	1.4715	98	.3487	.0539
					67.8 to 70.0	1.4702	104	.3242	.0522
25.9 to 29.3	1.4803	72	.4766	.0614	70.0 to 72.7	1.4693	108	.3110	.0514
29.3 to 32.3	1.4797	79	.4641	.0612	72.7 to 75.0	1.4692	108	.3094	.0512
32.3 to 35.4	1.4781	78	.4592	.0606					
35.4 to 38.5	1.4777	81	.4529	.0605	75.0 to 77.7	1.4685	111	.2962	.0503
38.5 to 40.3	1.4775	80	.4537	.0605	77.7 to 80.5	1.4672	116	.2802	.0492
40.3 to 42.9	1.4760	85	.4258	.0589	80.5 to 83.2	1.4673	115	.2817	.0491
42.9 to 44.8	1.4759		.4240		83.2 to 85.7	1.4670	119	.2762	.0490
44.8 to 47.7	1.4749	92	.3857	.0565	85.7 to 87.9	1.4663	120	.2671	.0481
47.7 to 49.7	1.4740	93	.3850	.0566					
49.7 to 52.2	1.4735	94	.3812	.0564	87.9 to 90.6	1.4659	120	.2632	.0476
					90.6 to 93.5	1.4652	124	.2543	.0471
52.2 to 55.0	1.4736	91	.3885	.0566	93.5 to 95.9	1.4642	128	.2450	.0464
55.0 to 57.8	1.4733	92	.3813	.0560	95.9 to 98.4	1.4625	134	.2298	.0452
57.8 to 59.5	1.4738		.3949		98.4 to 100	1.4626			

SERIES *C*

0 to 5.2	1.4934	60	0.6487	0.0710	47.8 to 51.8	1.4728	94	0.4315	0.0610
5.2 to 9.5	1.4931	58	.6827	.0726	51.8 to 54.7	1.4725	94	.4261	.0605
9.5 to 12.9	1.4917	57	.6948	.0733	54.7 to 57.6	1.4722	95	.4195	.0601
12.9 to 15.6	1.4889	61	.6751	.0730					
15.6 to 17.6	1.4868	61	.6559	.0721	57.6 to 62.6	1.4713	99	.3980	.0589
					62.6 to 65.9	1.4703	103	.3780	.0576
17.6 to 20.1	1.4871	61	.6724	.0729	65.9 to 69.6	1.4695	104	.3657	.0565
20.1 to 24.8	1.4855	61	.6698	.0727	69.6 to 72.3	1.4695	104	.3669	.0568
24.8 to 26.0	1.4833	63	.6385	.0715	72.3 to 76.0	1.4689	107	.3513	.0556
26.0 to 29.0	1.4818	71	.6157	.0710					
29.0 to 31.2	1.4811	74	.6031	.0704	76.0 to 79.2	1.4682	111	.3383	.0550
					79.2 to 82.1	1.4672	114	.3221	.0536
31.2 to 33.3	1.4798	72	.5866	.0692	82.1 to 86.8	1.4668	117	.3135	.0532
33.3 to 35.2	1.4798	----	.6063	----					
35.2 to 36.9	1.4798	----	.6188	----	86.8 to 88.1	1.4660	119	.3036	.0524
36.9 to 39.0	1.4794	69	.6174	.0707	88.1 to 91.1	1.4651	124	.2858	.0510
39.0 to 42.5	1.4787	81	.5857	.0712					
					91.1 to 93.8	1.4637	134	.2730	.0513
42.5 to 44.6	1.4761	81	.5209	.0660	93.8 to 100	1.4620	(123)	.2545	.0473
44.6 to 47.8	1.4736	90	.4475	.0618					

SERIES *D*

0 to 4.6	1.5002	45	1.054	0.0919	48.4 to 50.5	1.4753	93	0.5893	0.0745
4.6 to 8.7	1.5025	46	1.107	.0935	50.5 to 53.2	1.4742	95	.5633	.0729
8.7 to 12.5	1.4987	49	1.077	.0928	53.2 to 55.8	1.4734	99	.5347	.0714
12.5 to 16.6	1.4928	61	.9067	.0871					
16.6 to 20.1	1.4931	56	.9912	.0904	55.8 to 58.4	1.4733	100	.5285	.0710
					58.4 to 61.0	1.4719	105	.4842	.0684
20.1 to 23.1	1.4915	58	.9809	.0904	61.0 to 63.8	1.4719	104	.4891	.0686
23.1 to 25.5	1.4882	62	.9273	.0886	63.8 to 66.2	1.4720	102	.4985	.0690
25.5 to 27.6	1.4882	61	1.011	.0931	66.2 to 68.7	1.4721	104	.4994	.0694
27.6 to 29.8	1.4852	68	.9121	.0895					
29.8 to 31.9	1.4847	66	.9179	.0891	68.7 to 70.8	1.4716	103	.4827	.0682
					70.8 to 73.8	1.4697	112	.4279	.0648
31.9 to 33.9	1.4857	62	1.009	.0932	73.8 to 78.5	1.4693	115	.4087	.0633
33.9 to 36.0	1.4835	70	.8826	.0883	78.5 to 81.5	1.4692	124	.4137	.0639
36.0 to 38.0	1.4796	80	.7471	.0824	81.5 to 86.9	1.4689	117	.4045	.0634
38.0 to 40.0	1.4789	80	.7288	.0813					
40.0 to 42.0	1.4768	89	.6331	.0769	86.9 to 88.2	1.4676	121	.3832	.0620
					88.2 to 91.0	1.4670	122	.3726	.0611
42.0 to 44.2	1.4771	87	.6581	.0781	91.0 to 93.9	1.4658	128	.3452	.0592
44.2 to 48.4	1.4762	90	.6300	.0767	93.9 to 100	1.4643	135	.3193	.0577

TABLE 2.—*Physical properties of petroleum fractions*—Continued

SERIES *E*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at—	
			100° F	210° F
%			*Stoke*	*Stoke*
0 to 2.9	1.4970	60	1.293	0.1073
2.9 to 6.8	1.4994	55	1.370	.1094
6.8 to 10.2	1.4999	55	1.380	.1097
10.2 to 13.6	1.4926	66	1.148	.1023
13.6 to 16.2	1.4890	76	1.040	.0997
16.2 to 19.3	1.4856	81	.9322	.0953
19.3 to 21.7	1.4848	87	.9090	.0959
21.7 to 24.0	1.4828	86	.8629	.0924
24.0 to 27.3	1.4828	84	.8893	.0939
27.3 to 30.0	1.4819	87	.8513	.0921
30.0 to 32.5	1.4810	87	.8383	.0913
32.5 to 34.9	1.4802	89	.8209	.0905
34.9 to 37.0	1.4795	90	.8066	.0901
37.0 to 39.0	1.4786	94	.7753	.0892
39.0 to 40.7	1.4778	----------	.7569	----------
40.7 to 43.2	1.4777	96	.7605	.0889
43.2 to 45.4	1.4767	96	.7305	.0865
45.4 to 47.2	1.4760	97	.7095	.0855
47.2 to 49.1	1.4762	97	.7203	.0862
49.1 to 52.9	1.4758	98	.7037	.0853
52.9 to 55.0	1.4752	99	0.6814	0.0838
55.0 to 57.0	1.4750	99	.6899	.0844
57.0 to 58.7	1.4747	100	.6789	.0840
58.7 to 60.9	1.4746	100	.6796	.0842
60.9 to 62.8	1.4745	100	.6729	.0834
62.8 to 65.8	1.4737	103	.6528	.0829
65.8 to 67.8	1.4736	102	.6530	.0826
67.8 to 69.5	1.4733	----------	.6443	----------
69.5 to 71.5	1.4730	104	.6291	.0814
71.5 to 73.6	1.4730	104	.6318	.0815
73.6 to 75.3	1.4728	----------	.6237	----------
75.3 to 77.2	1.4724	107	.6112	.0806
77.2 to 84.8	1.4721	106	.6107	.0802
84.8 to 87.3	1.4714	110	.5794	.0789
87.3 to 89.8	1.4713	109	.5835	.0790
89.8 to 92.0	1.4711	113	.5535	.0773
92.0 to 94.4	1.4701	113	.5419	.0765
94.4 to 97.7	1.4692	118	.5204	.0762
97.7 to 100	1.4690	121	.5303	.0782

SERIES *F*

Charge	Refractive index, N_D^{25}	Kinematic viscosity index	Kinematic viscosity at—	
			100° F	210° F
0 to 4.4	1.4923	75	1.564	0.1280
4.4 to 9.3	1.4932	74	1.636	.1310
9.3 to 14.4	1.4917	76	1.554	.1282
14.4 to 19.0	1.4898	78	1.477	.1253
19.0 to 22.8	1.4898	78	1.492	.1259
22.8 to 27.6	1.4891	82	1.442	.1256
27.6 to 35.3	1.4867	82	1.385	.1224
35.3 to 39.0	1.4834	83	1.290	.1178
39.0 to 42.8	1.4821	86	1.241	.1166
42.8 to 46.4	1.4819	87	1.216	.1155
46.4 to 49.4	1.4791	----------	1.154	----------
49.4 to 52.9	1.4785	----------	1.106	----------
52.9 to 56.4	1.4774	94	1.047	0.1084
56.4 to 62.4	1.4771	94	1.042	.1077
62.4 to 65.3	1.4762	----------	.9944	----------
65.3 to 71.0	1.4761	97	.9765	.1053
71.0 to 75.3	1.4750	100	.9286	.1030
75.3 to 81.5	1.4745	98	.9259	.1019
81.5 to 84.4	1.4740	----------	----------	----------
84.4 to 89.7	1.4728	105	.8280	.0982
89.7 to 100	1.4714	115	.7332	.0948

TABLE 3.—*Physical properties of "key" fractions*

Series	Fraction	Charge	Molecular weight	Combustion analyses: Ratio moles H_2O/CO_2	Combustion analyses: Mass sample less mass C+H	In the formula $C_nH_{2n}+x$: n	In the formula $C_nH_{2n}+x$: x	Density at 100° F.	Density at 210° F.	Density at 77° F. (25° C.) (extrapolated)	Kinematic viscosity at 100° F.	Kinematic viscosity at 210° F.	Kinematic viscosity index	Refractive index N_D^{25}	Specific rotation $[\alpha]_D$ at 100° F. (dextro)	Boiling points at 1 mm of Hg.	Dispersion N_F-N_C at 25° C.	Aniline points
		%			g/g			g/ml	g/ml	g/ml	*Stoke*	*Stoke*				° C.		° C.
A 1	1 [a]	0.0 to 11.2	[d](380)	0.8359	0.0114	27.5	−9.0				0.6259	0.0655	36	1.5032				51.6
	3 [b]	20.2 to 34.7	380.6	.8689	.0024	27.6	−7.2	0.8920	0.8508	0.9006	.5785	.0656	56	1.4962	1.85	204	0.0104	71.6
	6	61.6 to 76.6	385.8	.9490	.0006	27.7	−2.8	.8657	.8257	.8741	.4887	.0606	64	1.4778	1.96	204	.0087	104.1
A 2	7	37.7 to 47.1	385.5	.9664	.0005	27.6	−1.86	.8516	.8119	.8600	.3281	.0511	93	1.4717	1.10	204.5	.0086	107.2
	Residue	83.3 to 100	385.2	.9838	.0019	27.5	−0.89	.8342	.7941	.8426	.2306	.0438	123	1.4647	.31	205.6		
A 3	6 [b]	50.2 to 59.3	386.6	.9941	.0005	27.6	−0.32	.8259	.7857	.8343	.2010	.0414	136	1.4609	.11	208.2	.0083	109.7
	9	75.2 to 83.2						.8227	.7819	.8312	.1908	.0404	141	1.4604	.05		.0084	112.2
	Residue [c]	83.2 to 100	392.4	1.0059	.0003	28.0	+0.35	.8193	.7782	.8278	.1808	.0398	149	1.4587		206.3	.0083	113.3
B	1	.0 to 6.6	395.4	.9046	.0032	28.5	−5.4	.8766	.8357	.8851	.5084	.0630	70	1.4875	1.34	212.4		
	7	29.3 to 32.3	398.2	.9382	.0000	28.6	−3.54	.8655	.8247	.8740	.4641	.0612	79	1.4797	1.79	211.5		
	21	63.5 to 65.5	401.0	.9688	.0000	28.7	−1.80				.3612	.0548	96	1.4721	1.22			
	34	95.9 to 98.4	406.4	.9943	.0000	29.0	−0.34	.8274	.7880	.8357	.2298	.0452	134	1.4625	.21	217.5		
C	1 [b]	.0 to 5.2	400.2	.8822	.0036	29.0	−6.8	.8866	.8464	.8950	.6487	.0710	60	1.4934	1.20	218.0	.0104	81.9
	15	39.0 to 42.5	412.9	.9493	.0006	29.6	−3.02	.8657	.8260	.8740	.5857	.0712	81	1.4787	1.79	219.4	.0087	106.5
	23 [b]	65.9 to 69.6	417.2	.9737	.0005	29.9	−1.58	.8470	.8060	.8556	.3657	.0565	104	1.4695	.82	222.7	.0085	112.1
	Residue	93.8 to 100	424	.9956	.0002	30.2	−0.27	.8279	.7873	.8364	.2545	.0472	(123)	1.4620	.11	226.1	.0082	116.4
D	2	4.6 to 8.7	421	.8523	.0043	30.5	−9.0	.9000	.8599	.9084	1.107	.0935	46	1.5025	1.06	231.2	.0116	53.7
	17	44.2 to 48.4	444	.9585	.0007	31.8	−2.60	.8597	.8204	.8679	.6300	.0767	90	1.4762	1.22	232.7	.0087	111.4
	30	81.5 to 86.9	451.5	.9796	.0021	32.2	−1.31	.8420	.8009	.8504	.4045	.0634	117	1.4689	.31	235.9	.0087	114.9
	Residue	93.9 to 100	458.6	.9949	.0000	32.7	−0.33	.8299	.7897	.8383	.3193	.0577	135	1.4643	.04	240.7	.0083	121.3
E	3	6.8 to 10.2	431.3	.8677	.0035	31.2	−8.3	.8948	.8553	.9031	1.380	.1097	55	1.4999	.90	245.4	.0107	81.9
	9	24.0 to 27.3	452	.9266	.0008	32.5	−4.8	.8704	.8305	.8788	.8893	.0939	84	1.4828	.87	249.4	.0092	105.1
	20	49.1 to 52.9	477	.9598	.0002	34.2	−2.75	.8569	.8179	.8651	.7037	.0853	98	1.4758	.67	246.4	.0086	115.3
	33	77.2 to 84.8	481.7	.9741	.0015	34.4	−1.78	.8503	.8106	.8587	.6107	.0802	106	1.4721	.39	250.4	.0086	117.5
	Residue	97.7 to 100	495.3	.9820	.0002	35.4	−1.27	.8415	.8018	.8499	.5303	.0782	121	1.4690	.06	260.0	.0084	122.3
F	1	.0 to 4.4	511	.9011	.0040	36.8	−7.4	.8827	.8432	.8910	1.564	.1280	75	1.4923	.45	269.5	.0098	101.1
	7	27.6 to 35.3	519	.9199	.0009	37.4	−6.0	.8747	.8362	.8828	1.385	.1224	82	1.4867	.51	269.5	.0096	107.4
	16	65.3 to 71.0	523	.9598	.0004	37.5	−3.02	.8573	.8180	.8655	.9765	.1053	97	1.4761	.30	271.7	.0086	120.7
	20	84.4 to 89.7	525	.9721	.0010	37.6	−2.10	.8513	.8130	.8591	.8280	.0982	105	1.4728	.09	273.5	.0085	123.0
	Residue	89.7 to 100	537	.9747	−.0003	38.4	−1.95	.8464	.8075	.8545	.7332	.0948	115	1.4714	.00	275.6	.0085	125.2

[a] This fraction was analyzed for sulfur by C. E. Waters of this Bureau, who found it contained 0.08% of S. It was also analyzed for nitrogen and found to contain none, by R. T. Milner of the Bureau of Fixed Nitrogen, U. S. Department of Agriculture. The loss found in the combustion analysis is, therefore, attributable principally to oxygen.

[b] Iodine numbers were determined on these fractions by the Detergents Section of this Bureau. For fractions $A_1$3, $A_2$6, *C*1, and *C*23, the iodine numbers were 21.4, 0.96, 18.1, and 1.9, respectively.

[c] The residues from the extraction all contained small quantities of wax. The wax from fraction A_3 residue was removed by filtration. It had a refractive index $N_D^{80}=1.429$ and melting point=58° C. This crystalline material appears to be a mixture of normal paraffin hydrocarbons which had escaped removal in the original dewaxing process.

[d] Estimated value, fraction lost.

The percentage of the charge represented by each of the fractions was calculated, not on the basis of the oil charged into the extractors, but on the basis of the total weight of the fractions recovered. The weight of the oil recovered agreed with that charged into the extractor within a few grams, except for series *D*, where a break in the extractor caused a loss of 163 g.

XI. CONCLUSION

An examination of the physical constants of the oil fractions for series A_1, A_2, and A_3, shows that an excellent separation with respect to type of molecule has been obtained. The kinematic viscosities at 100° F vary from 74 to 18 centistokes, viscosity indices from 35 to 149, refractive indices from 1.5032 to 1.4587, the value of x in the equation C_nH_{2n+x} from -9 to $+0.35$, while the number of carbon atoms to the molecule remains substantially constant. The separation for the charges of higher molecular weight is not quite so satisfactory, and some separation with respect to molecular weight, as well as with respect to type of molecule, is evident. This is probably due to the fact that these higher boiling fractions still had somewhat of a boiling range, as indicated in figure 2.

The authors express their gratitude for the advice and encouragement of F. D. Rossini during this investigation. They also express their gratitude for the advice of M. R. Fenske, of Pennsylvania State College, whose suggestion of the type of extractor column used in this investigation proved valuable.

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WASHINGTON, September 2, 1936.

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RELATIONSHIPS BETWEEN PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION OF LUBRICATING OIL FRACTIONS[1]

By Beveridge J. Mair and Charles B. Willingham[2]

ABSTRACT

A correlation of the physical properties of a series of petroleum fractions in the lubricating-oil region with each other and with the physical properties of synthetic hydrocarbons of high molecular weight has been made. The petroleum fractions had been extensively separated by distillation and extraction and their empirical formulas determined. The following properties were compared: densities, specific refractions, optical activities, specific dispersions, viscosities, viscosity indices, aniline points, and boiling points.

It appears that the least soluble portion of the oil, that is, the material corresponding to the most highly refined product obtained by any good solvent extraction process, consists substantially of naphthenes (cycloparaffins) containing from one to about three rings to the molecule, together with the necessary alkyl radicals. The somewhat more soluble portion consists of naphthenes with more rings, together with some unsaturated hydrocarbons and possibly some aromatic hydrocarbons. There is no evidence whatever for the existence of iso or branched-chain paraffins.

Because of the similar solubility relations, it is possible that in the extraction processes as used at the present time one-ring aromatic hydrocarbons are being discarded to waste along with the undesirable naphthenes containing about six rings to the molecule. This is a point well worth investigating, since these one-ring aromatic hydrocarbons may be a valuable constituent for good lubricating oil.

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[2] Research Associates at the National Bureau of Standards, representing the American Petroleum Institute.

I. INTRODUCTION

The literature dealing with the constitution of the lubricant fraction of petroleum has recently been reviewed by Mikeska [1] [3] and Rossini [2]. An examination of these and other articles shows a considerable divergence of opinion as to what types of hydrocarbons are present and what relationships exist between chemical constitution and physical properties. The feeling of doubt which exists regarding the chemical nature of the high-boiling fractions of petroleum is exemplified by the following quotation from a recent paper by Lane and Garton [3]: "From the standpoint of pure chemistry the use of 'paraffin', 'naphthene', and similar terms as applied to the heavy ends of crude petroleum is still less justified. There are virtually no published data on the higher boiling fractions of crude oil which would indicate in a reliable manner the chemical nature of the compounds present."

One of the factors which has materially retarded knowledge in this field has been the lack of information concerning the physical properties of synthetic hydrocarbons of high molecular weight. Recently a large number of hydrocarbons of high molecular weight have been synthesized, principally by Mikeska [1], and many of their physical properties determined, so that a direct comparison of their properties with those of petroleum fractions is now possible.

In this laboratory there have recently been prepared from a mid-continent crude petroleum by extensive distillation and extraction a series of lubricating-oil fractions, which are perhaps more homogeneous with respect to type of molecule and molecular weight than any fractions hitherto obtained from lubricating oil. In the expectation of clearing up some of the existing differences of opinion, and in extending the knowledge of the chemical constitution of the lubricant fraction, this paper presents a correlation and comparison of the physical properties of these fractions with each other, and with those of synthetic hydrocarbons of high molecular weight.

II. ORIGIN AND HISTORY OF THE PETROLEUM FRACTIONS

The origin of the lubricating-oil stock was well no. 6 of the South Ponca Field, Kay County, Okla. Before receipt at this Bureau, the portion of the crude petroleum containing the lubricating oil was fractionally distilled in "vacuo" by the Sun Oil Co. at Philadelphia. Its treatment after receipt at this Bureau is described in detail elsewhere [4, 5] and is illustrated diagrammatically in figure 1. Briefly, this treatment consisted in the preparation of a "water-white" oil by extraction with sulphur dioxide, by removal of wax, and by filtration through silica gel. This water-white oil was then fractionally distilled until substantially constant-boiling fractions were obtained. Charges with narrow boiling range were then extracted with acetone in 14-meter columns, each charge being separated into about 25 to 30 fractions. A number of fractions from six of the charges (designated as series *A*, *B*, *C*, etc., in fig. 1) were selected as key fractions and their empirical formulas, together with a large number of physical proper-

[3] The figures given in brackets here and elsewhere in the text correspond to the numbered references at the end of this paper.

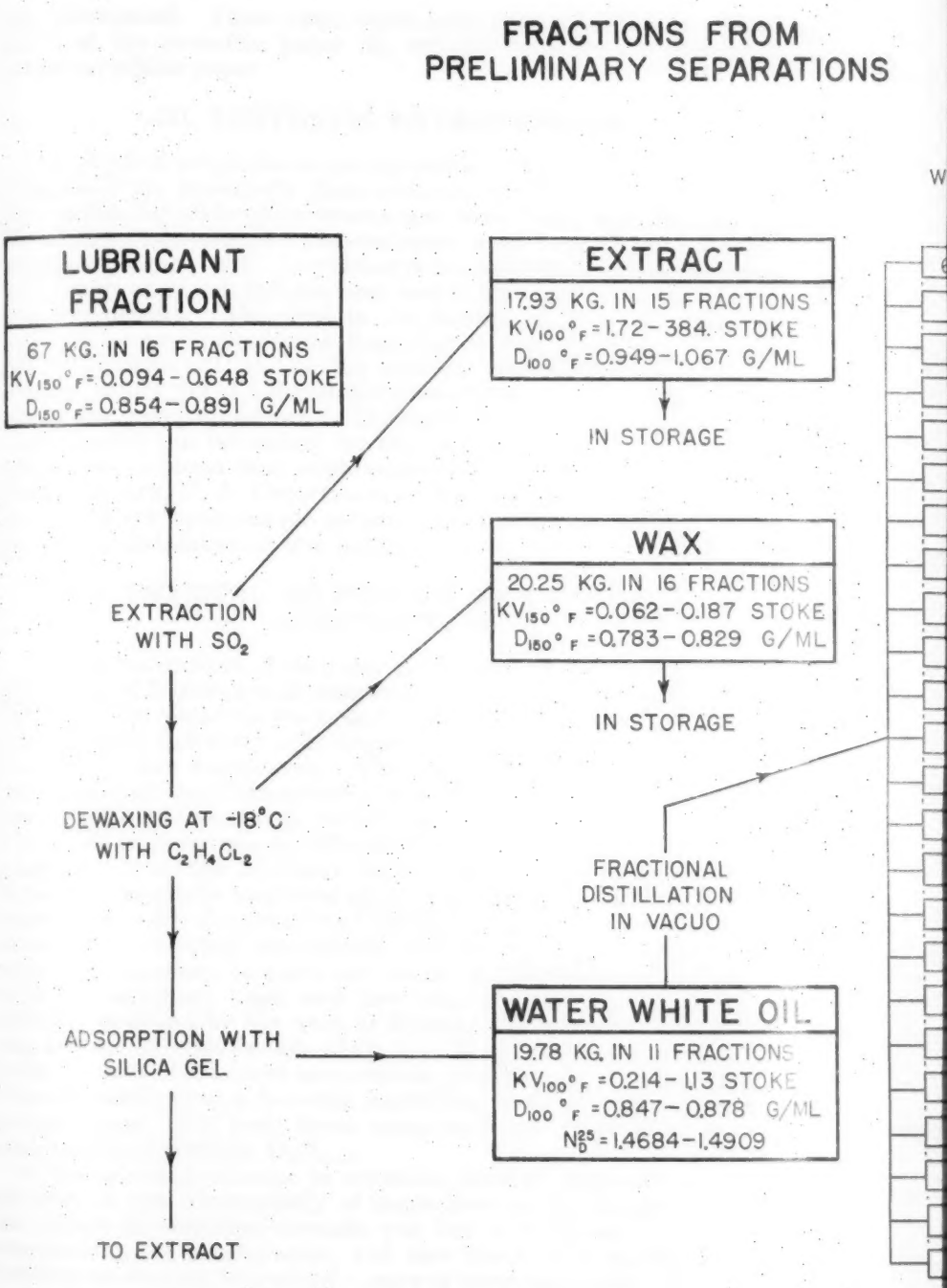
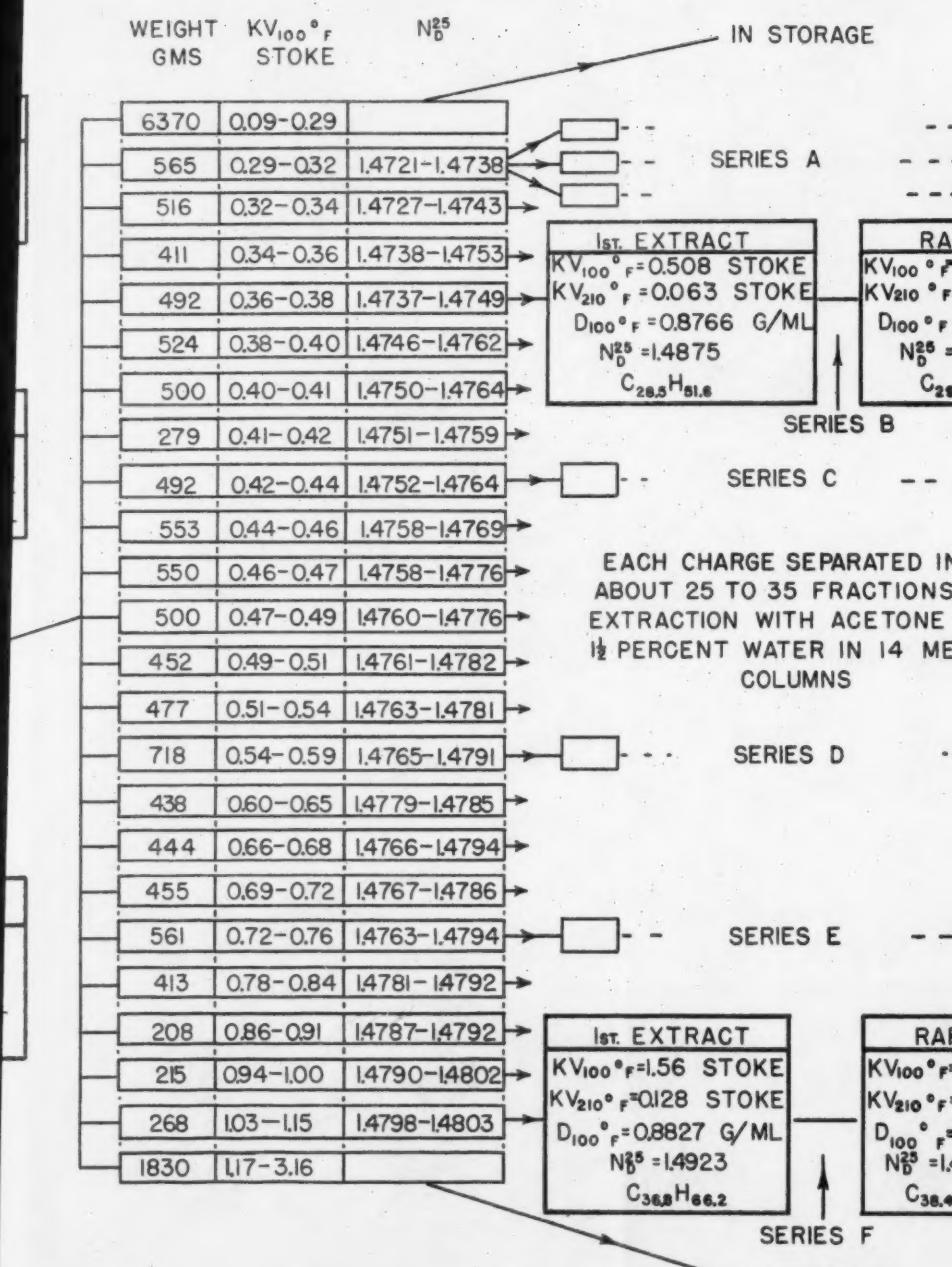

FRACTIONS FROM
PRELIMINARY SEPARATIONS
LUBRICANT FRACTION
67 KG. IN 16 FRACTIONS
KV150°F = 0.094 - 0.648 STOKE
D150°F = 0.854 - 0.891 G/ML
EXTRACT
17.93 KG. IN 15 FRACTIONS
KV100°F = 1.72 - 384. STOKE
D100°F = 0.949 - 1.067 G/ML
IN STORAGE
WAX
20.25 KG. IN 16 FRACTIONS
KV150°F = 0.062 - 0.187 STOKE
D150°F = 0.783 - 0.829 G/ML
IN STORAGE
EXTRACTION WITH SO2
DEWAXING AT -18°C WITH C2H4Cl2
FRACTIONAL DISTILLATION IN VACUO
WATER WHITE OIL
19.78 KG. IN 11 FRACTIONS
KV100°F = 0.214 - 1.13 STOKE
D100°F = 0.847 - 0.878 G/ML
N25D = 1.4684 - 1.4909
ADSORPTION WITH SILICA GEL
TO EXTRACT

FIGURE 1.—*Chart showing treatment and*

ONS

CHARGES FOR EXTRACTION

FRACTIONS FROM EXTRACTION



treatment and disposition of lubricating oil fractions.

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FROM
ION

E

RAFFINATE
KV_{100} °F 0.230 STOKE
KV_{210} °F = 0.045 STOKE
D_{100} °F = 0.8274 G/ML
N_D^{25} = 1.4625
$C_{29.0}H_{57.7}$

B

ATED INTO
CTIONS BY
ETONE PLUS
14 METER

RAFFINATE
KV_{100} °F = 0.733 STOKE
KV_{210} °F = 0.095 STOKE
D_{100} °F = 0.8470 G/ML
N_D^{25} = 1.4714
$C_{38.4}H_{74.7}$

F

GE

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ties, determined. These data, which have been published in tables 2 and 3 of the preceding paper [5], are the basis for the correlation contained in this paper.

III. SYNTHETIC HYDROCARBONS

The physical properties of the synthetic hydrocarbons used in this comparison are principally those reported by Mikeska [1]. In addition, values for 16-butylhentriacontane from Suida and Planckh [6], dimethyl-9,12-di-*n*-hexyl-9,10-octadecane from Lerer [7], 1,1-dicyclohexylhexadecane and 1-cyclohexyl-2-hexahydrobenzylheptadecane from Landa and Cech [8] have been used in the charts of specific refraction and density. Also used in the density chart is the value for 1-phenyl-2-benzylheptadecane from Landa and Cech [8]. In addition to Mikeska's [1] values, the viscosity and viscosity-index charts contain values for 1,1-dicyclohexylhexadecane and 1-cyclohexyl-2-hexahydrobenzylheptadecane. The aniline-point chart contains values determined in this laboratory for two normal paraffins. The *n*-nonacosane was prepared from apple cuticle by K. S. Markley, Bureau of Plant Industry, U. S. Department of Agriculture. The *n*-dotriacontane was a synthetic sample prepared by Y. Delcourt [9] and further purified by distillation in this laboratory.

IV. PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

In his investigations of the lubricant portion of petroleum, Mabery [10] obtained fractions with empirical formulas ranging from C_nH_{2n} to C_nH_{2n-30}. He tested his fractions for unsaturation, and, finding none, attributed the deficiency in hydrogen from the formula C_nH_{2n+2} to the presence of ring compounds. This deficiency of hydrogen in well refined oils of the Pennsylvania type is usually attributed to the presence of naphthene rings rather than of aromatic rings. However, it is known to be extremely difficult to remove aromatic hydrocarbons completely from the lubricant fraction, and the term "more naphthenic" as frequently employed signifies nothing more than an increasing deficiency of hydrogen in the formula $C_nH_{2n\pm z}$. Yet, in attempting to relate the chemical constitution and the physical properties, it is extremely important to know how much of this deficiency is attributable to naphthene rings and how much to aromatic rings. For example, as shown by the work of Mikeska [1], an aromatic with one ring and a long paraffin side chain may be expected to have a much lower viscosity and a lower temperature coefficient of viscosity (higher viscosity index) than a four-ring naphthene with the same number of carbon atoms. Yet both these compounds are represented by the same empirical formula, C_nH_{2n-6}.

In the following attempt to correlate physical properties and constitution, it was consequently of importance to decide how much of the change in empirical formula was due to a change in aromatic concentration or unsaturation, and how much to a separation into fractions containing, respectively, more or fewer naphthene rings.

Several methods which utilize such physical properties as molecular volumes (Davis and McAllister [11]), specific refractions, specific dispersions, and aniline points (Vlugter, Waterman, and Van Westen

[12]) have been used by other investigators to detect the presence of aromatics, or to determine the number of naphthenic rings in petroleum fractions. But these methods usually involved a considerable extrapolation from the properties of synthetic hydrocarbons of low molecular weight to those of high molecular weight, and it was difficult to say how reliable they were. Now, however, it is possible to check these methods with synthetic hydrocarbons of high molecular weight and arrive at a reliable picture as to the composition of the fractions under investigation.

1. DENSITIES

In figure 2 is shown a plot of the densities of a number of synthetic hydrocarbons of diverse types with respect to the number of carbon atoms they contain. Also represented by circles in the same figure are the densities of the key fractions from petroleum. The figures within these circles denote the value for x in the formula C_nH_{2n+x}. The key fractions resulting from the extraction of each charge are connected with arrows, which denote the order of their extraction. An examination of figure 2 shows that monocyclic aromatics have lower densities than bicyclic naphthenes, although the value for x in the formula C_nH_{2n+x} is -6 for monocyclic aromatics and -2 for bicyclic naphthenes. This suggests that a consideration of the values for x in conjunction with the densities may be used to determine whether an oil is composed of aromatics or naphthenes. It is evident that the densities of the less soluble key fractions are, for given values of x, in fair agreement with those of the corresponding cyclohexane derivatives, but are much too high to be accounted for on the supposition that they are composed of monocyclic aromatics, or their mixtures with isoparaffins or naphthenes. For the more soluble fractions the densities are also higher for given values of x than those of the corresponding aromatics, which suggests that they also contain naphthenes. However, the absence of synthetic naphthenes with corresponding values of x, makes a direct comparison impossible, and the fact that in some cases the density is not so markedly higher than that of the corresponding aromatics suggests that they may also contain some aromatic or unsaturated hydrocarbons. This is borne out by a consideration of their other properties.

2. SPECIFIC REFRACTIONS

An important method for detecting the presence of aromatics or unsaturated hydrocarbons in petroleum fractions, in which use is made of the specific refraction, has been employed by Vlugter, Waterman, and Van Westen [12]. These authors point out that if the Lorentz-Lorenz specific refraction, $\frac{n_D^2-1}{n_D^2+2}\cdot\frac{1}{d}$, is considered, aromatics and isoparaffins have high specific refractions, while for naphthenes the specific refraction is lower and decreases as the number of rings in the naphthene is increased. Vlugter, Waterman, and Van Westen in this work have computed theoretical values of the specific refraction for paraffins and naphthenes of high molecular weight from Eisenlohr's values for the atomic refractions of carbon (2.418) and hydrogen (1.100). This method has, however, been criticized by Griffith and Hollings [13] who state, "We do not feel that agreement

between observed and calculated figures for the very few known hydrocarbons cited is sufficiently good to justify the extrapolation of the curves to include mixtures of widely different molecular weight. The fact that aromatic hydrocarbons are known not to give experimental results in agreement with those calculated is also significant."

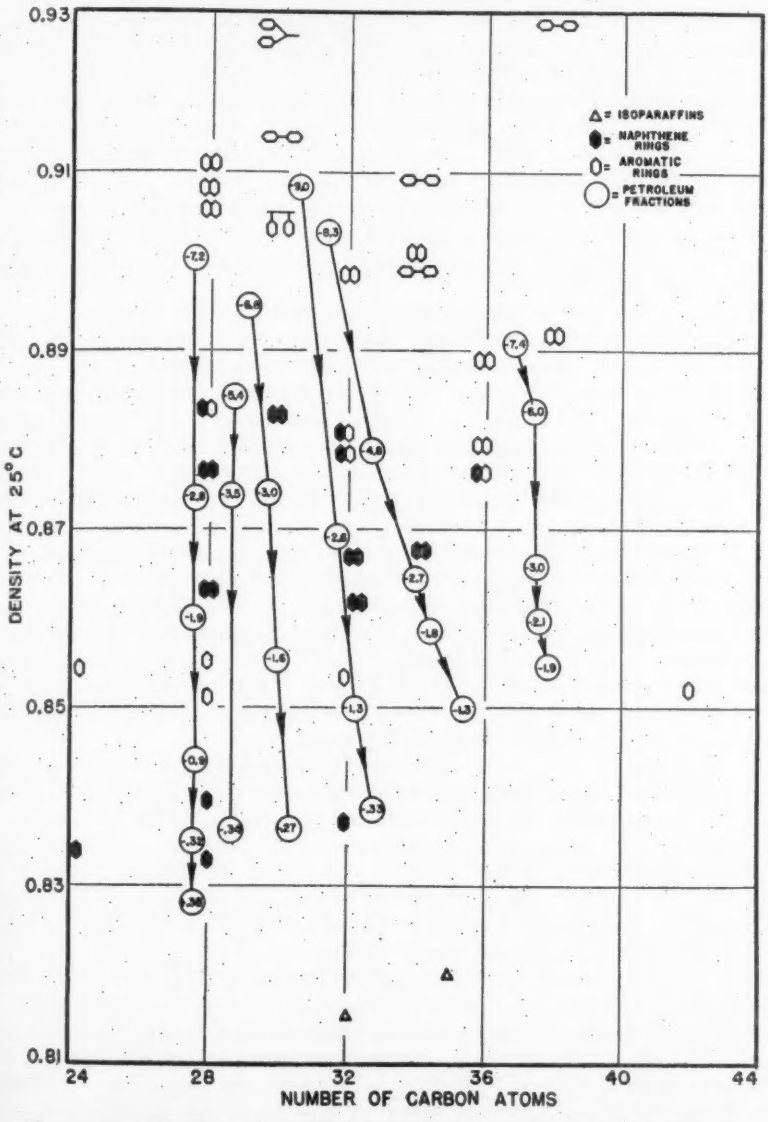


FIGURE 2.—*Densities of synthetic hydrocarbons and petroleum fractions.*

It is now possible to answer this criticism by calculating the specific refraction of a number of synthetic hydrocarbons in the region in which we are interested. This shows that Vlugter, Waterman, and Van Westen's curves for naphthenes represent the facts remarkably well, and by the use of the method one can determine which of the

fractions from petroleum are free from aromatics and unsaturated hydrocarbons.

In figure 3 are shown theoretical curves similar to those of Vlugter, Waterman, and Van Westen giving the variation in specific refraction with the number of carbon atoms for paraffins and mono-, di-, and tricyclic naphthenes. In addition, a curve for monocyclic aromatics is included, computed on the assumption that a benzene ring causes an increment of 5.1[4] in the molecular refraction. On the left half of the figure are plotted values for the specific refractions of the synthetic hydrocarbons. Although there is very considerable variation in the specific refraction of the aromatics, it can be seen that, as stated by Vlugter, Waterman, and Van Westen [12] the aromatics, together with the isoparaffins, have high specific refractions. The values for three out of the four monocyclic naphthenes average close to the theoretical curve. The one with 24 carbon atoms is distinctly out of line. For the dicyclic naphthenes the agreement with the theoretical curve is remarkably good.

On the right half of the figure are plotted specific refractions of the key fractions from petroleum. As before, the fractions from each individual charge are connected with arrows which denote the order of their extraction. The figures within the circles represent the value of x in the formula C_nH_{2n+x}. Unlike the density and the refractive index, which show a continuous decrease as the ratio of hydrogen to carbon increases, the specific refractions go through minima. Presumably there is some fundamental change in the constitution of the fractions as these minima are passed. The specific refractions of the first, and in some cases the second, key fractions are much too high to be accounted for on the supposition that they are naphthenes. Lines are drawn from these fractions to points which indicate approximately what should be the values of their specific refractions if they were purely naphthenic. On the other hand, if they were purely aromatic, their specific refractions would be much higher. For all the other fractions the agreement between the specific refractions and the theoretical curves for naphthenes is remarkably good.

In addition to aromatic hydrocarbons, unsaturated hydrocarbons and nonhydrocarbon materials have high specific refractions, and one or all of these might be responsible for the high specific refractions of the first, and in some instances second, key fractions. Two of these fractions designated *A* and *C* were examined in greater detail in an attempt to decide which of these types of substances was chiefly responsible. As shown by the combustion analysis, fractions *A* and *C* contained only 0.2 percent and 0.36 percent of oxygen (or other nonhydrocarbon materials), and it was evident that such a small percentage could not account for any appreciable part of the abnormality in specific refraction. Iodine numbers showed considerable unsaturation *A* and *C* giving, respectively, iodine numbers of 21.4 and 18.1, which corresponds to 0.32 and 0.28 double bond to the molecule. Eisenlohr has shown that one double bond to the molecule produces (on the average) an increment in molecular refraction of 1.707, so that the presence of 0.32 and 0.28 double bond to the molecule would cause increments of 0.548 and 0.487 in molecular refractions, which correspond for fractions *A* and *C* to increments of 0.00154 and 0.00121 in the

[4] This value was arrived at from a consideration of the molecular refraction of benzene, toluene, *o*-, *m*-, and *p*-xylene, and the three trimethylbenzenes.

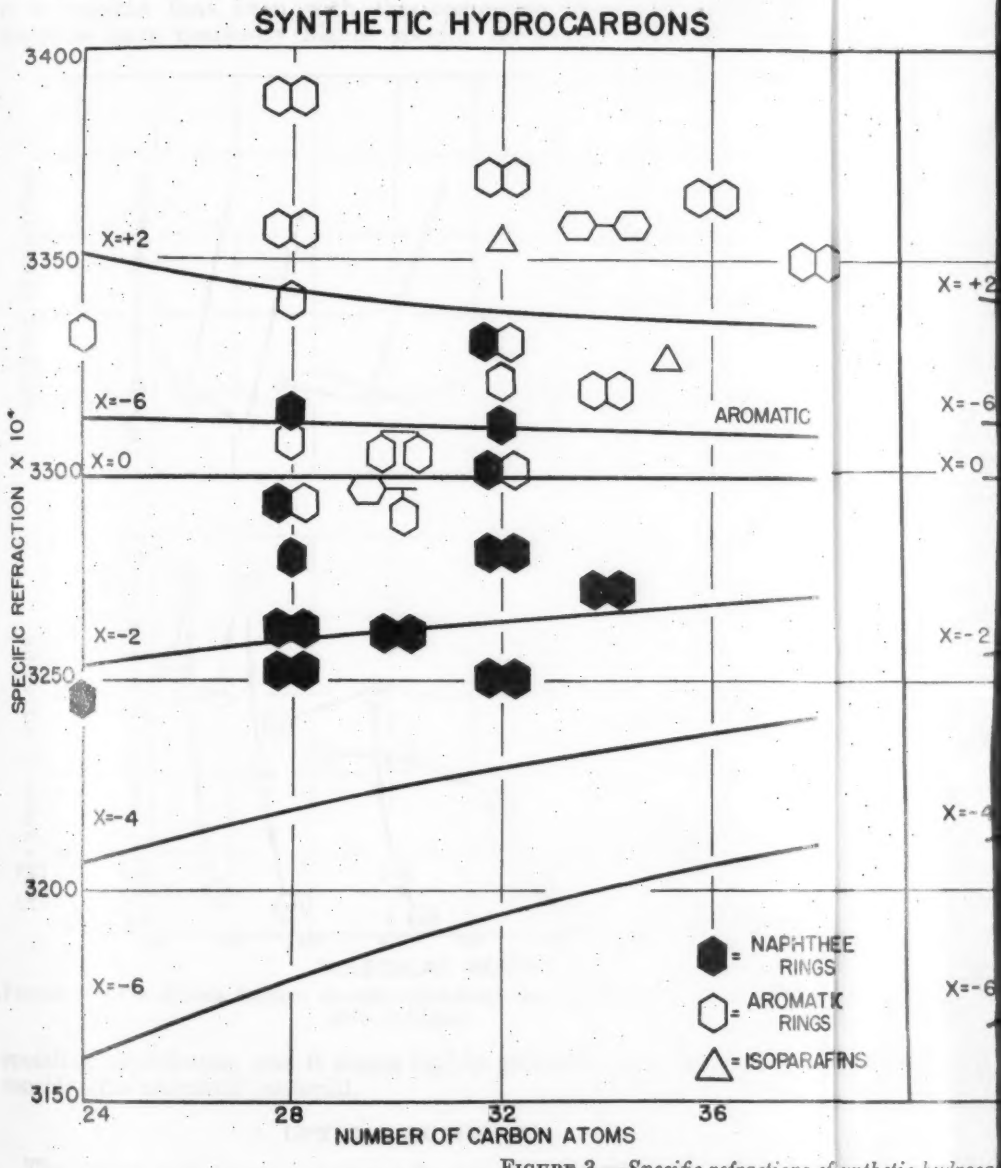
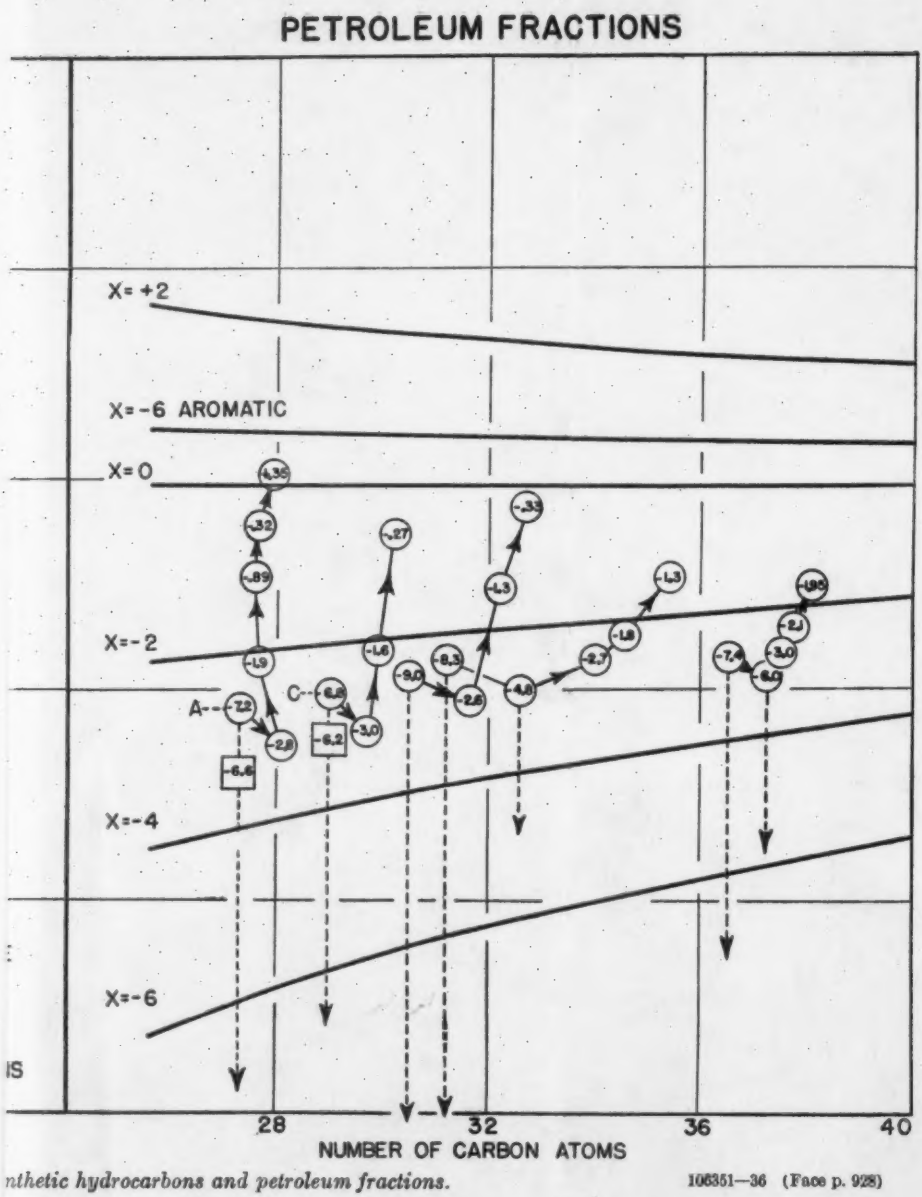


FIGURE 3.—*Specific refractions of synthetic hydroca*



nthetic hydrocarbons and petroleum fractions.

105351—36 (Face p. 928)

SPECIFIC REFRACTION X 10^4

UNIV. OF WICH.

SYNTHETIC HYDROCARBONS
NUMBER OF CARBON ATOMS

specific refraction. By subtracting these values from the specific refractions of A and C, one should obtain the specific refractions of A and C if they had contained no unsaturated material. The positions of A and C corrected in this manner are designated in figure 3 by squares, the figures within the squares indicating the x values for these fractions if they had contained no unsaturated material. It is evident that even with this correction for unsaturation the fractions have markedly higher specific refractions than the corresponding naphthenes, and it seems highly probable that they contain considerable aromatic material.

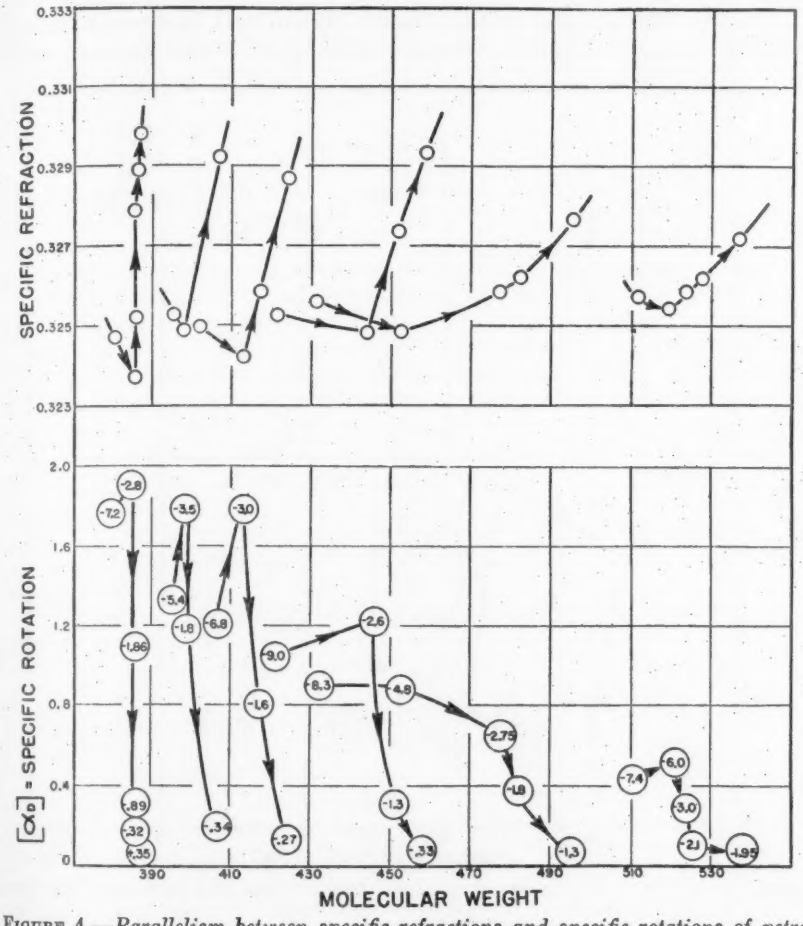


FIGURE 4.—*Parallelism between specific refractions and specific rotations of petroleum fractions.*

3. OPTICAL ACTIVITIES

The optical activity of petroleum fractions is of importance since its study may shed considerable light not only on the constitution of petroleum but also on its origin. In figure 4 are shown plots of the specific rotation and specific refraction of the key fractions with respect to molecular weight. It is evident that the optical activities decrease

with increasing molecular weight. It is also apparent that the activity is least for those fractions with the smallest number of naphthene rings but increases rapidly with increase in the average number of naphthene rings. There is a striking parallelism between specific rotation and specific refraction, the specific refraction passing through minima for those fractions where the rotations pass through maxima. Since there is no connection between specific refraction and specific rotation for substances in general, the parallelism pointed out here must have some significance peculiar to the composition of petroleum. As pointed out previously, the first fractions contain unsaturated hydrocarbons and probably aromatic hydrocarbons, and consequently it seems reasonable

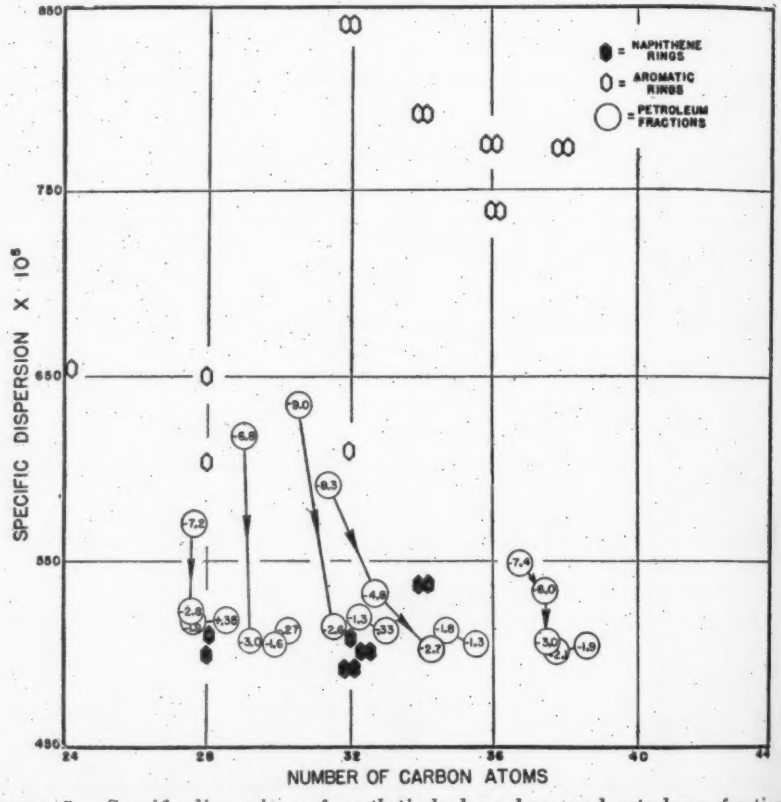


FIGURE 5.—*Specific dispersions of synthetic hydrocarbons and petroleum fractions.*

to suppose that the decrease in activity is due to the presence of unsaturated hydrocarbons or aromatics. If it is due to aromatic hydrocarbons it is interesting to speculate as to whether all aromatics in petroleum have low optical activities, or, as in the case of naphthenes, whether the activity depends on the number of rings in the molecule.

4. SPECIFIC DISPERSIONS

Another property used by Vlugter, Waterman, and Van Westen [12] for detecting the presence of aromatic hydrocarbons in petroleum oils is the specific dispersion. These authors point out that, as with

specific refraction, the specific dispersion is highest for aromatics and lowest for naphthenes, decreasing with increase in the number of naphthene rings. In figure 5 are plotted values for the Lorentz-Lorenz specific dispersion

$$\frac{n^2_{F-1}}{n^2_{F+2}}-\frac{n^2_{c-1}}{n^2_{c+2}} \cdot \frac{1}{d}$$

for the key fractions from petroleum and for some of Mikeska's [1] synthetic hydrocarbons.[5] It is quite clear from a consideration of this property also that the first, and in a few instances the second, key fractions contain some aromatic or unsaturated hydrocarbons, but that in the remainder of the fractions the deviations of x in the formula C_nH_{2n+x} from the value $+2$ is due to the presence of naphthene rings.

5. ANILINE POINTS

In figure 6 is shown a plot of the aniline points[6] of the key fractions from petroleum with respect to the number of carbon atoms, fractions from each series being connected with arrows which denote the order of their extraction. There are also included values for a number of synthetic hydrocarbons. Lines drawn through each type of synthetic hydrocarbon indicate approximately the change in aniline point with molecular weight for that type. Unfortunately, aniline points for only three synthetic naphthenes are available. The aniline points for the two synthetic monocyclic naphthenes are somewhat lower (about 5° C) than the aniline points of the corresponding petroleum fractions, while the aniline point for the synthetic dicyclic is about 1° lower than that of the corresponding petroleum fractions. It is doubtful whether these differences are significant, as they may be due to differences in the technique employed in determining the aniline points—such as purity of aniline, etc. As with the other properties, the aniline points of the first key fractions are abnormal, being too low to be accounted for on the supposition that only naphthenes are present.

These data make evident the extreme importance of extracting fractions with a very narrow range of molecular weights if it is hoped to separate the various types of molecules. For example, judging from the aniline points of the key fractions, the aniline point of a dicyclic naphthene of 30 carbon atoms is about the same as that of a monocyclic with 28 carbon atoms. To effect a separation of monocyclic naphthenes from dicyclic naphthenes, by the use of solvents similar in behavior to aniline, it is almost necessary to use fractions composed entirely of hydrocarbons with the same number of carbon atoms. A monocyclic naphthene with 32 carbon atoms has about the same solubility as a monocyclic aromatic with 42 carbon atoms, so that even the separation of monocyclic aromatics from monocyclic naphthenes requires that the distillation range be not too wide. With

[5] The dispersion values on the petroleum fractions, and those of Mikeska [1] on synthetic hydrocarbons, were obtained with an Abbe refractometer which gave values of n_F-n_c instead of n_F and n_c, the properties required in this instance. To obtain the actual values of n_F and n_c use was made of Hartmann dispersion paper on which refractive indices for the different wave lengths are supposed to give a straight line. The validity of this procedure was checked by measuring the dispersion (n_F-n_c) for hexane, octane, and benzene, using the value for n_D given in International Critical Tables, and computing the values of n_F and n_c. The results agreed with the International Critical Tables values within 1 in the fourth decimal place for octane and benzene, and deviated by 2 in the fourth place for the F line of hexane. This method of calculation was suggested by C. P. Saylor of this Bureau.

[6] The aniline point is the temperature of complete miscibility of equal volumes of oil and aniline.

increase in the average number of naphthene rings in the key fractions the aniline point decreases and an extrapolation from the fractions composed of mono- and dicyclic naphthenes to the polycyclic naphthenes leads to the conclusion that the solubilities of six-ring naphthenes would not be far removed from the solubilities of monocyclic aromatics. So, to effect a separation of those classes by extraction

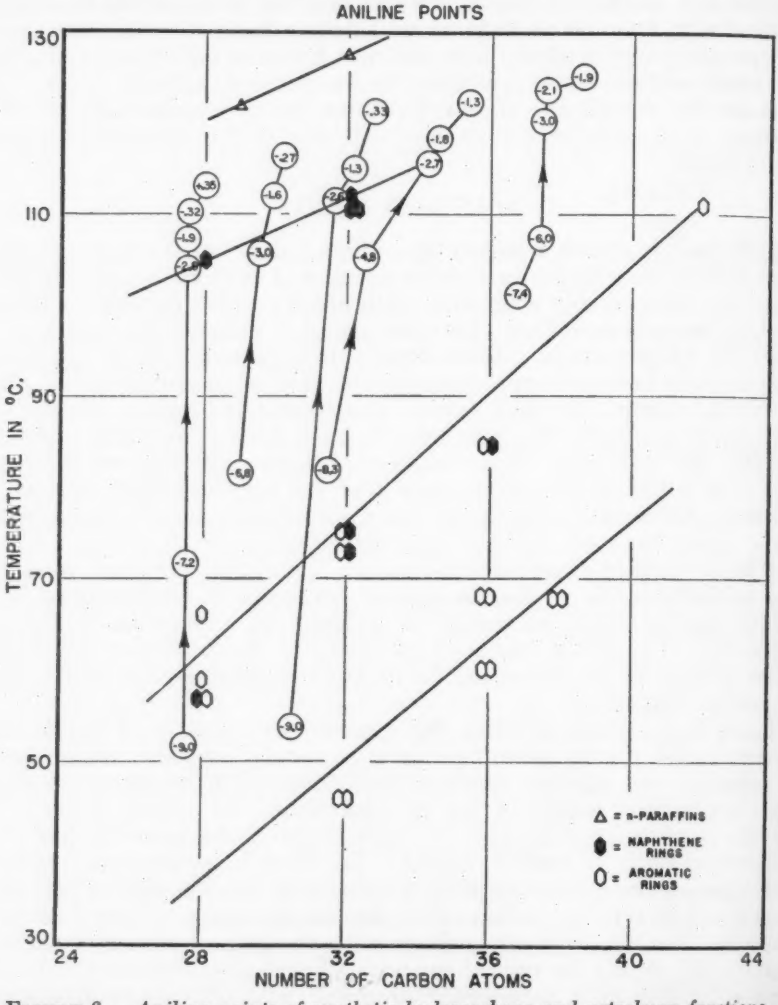


FIGURE 6.—*Aniline points of synthetic hydrocarbons and petroleum fractions.*

would require very narrow distillation fractions. This point will be referred to later.

6. VISCOSITY INDICES

The relationship between viscosity, the temperature coefficient of viscosity, and constitution have been investigated by many chemists, and is now much better understood than a few years ago. Hugel [14] and Mikeska [1], attacking the problem from the synthetic angle, have

shown that increasing the degree of cyclization causes an increase in viscosity and a decrease in viscosity index. Davis and McAllister [11] found that a linear relationship exists between the viscosity index of an aromatic-free oil and the percentage of carbon atoms in naphthene rings, the viscosity index decreasing with increase in the per-

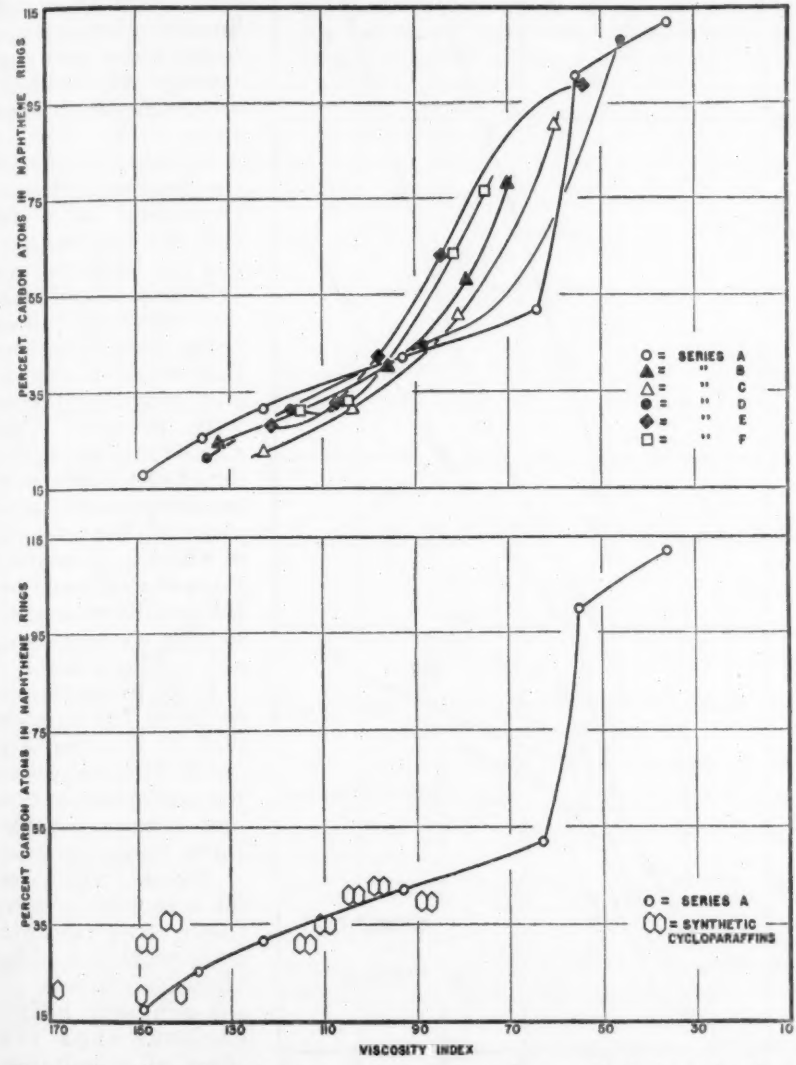


FIGURE 7.—*Viscosity indices of synthetic hydrocarbons and petroleum fractions.*

centage of carbon atoms in naphthene rings. They pointed out that the first extracts which they obtained from a Pennsylvania oil deviated from this linearity and explained this on the assumption that the first extracts contained aromatic or unsaturated hydrocarbons. It was of interest to test the relationship found by Davis and McAllister [11] with the key fractions obtained in this investigation. In the upper half of figure 7 is shown a plot of the percentage of carbon atoms

in naphthene rings (calculated from the empirical formulas on the assumption of six carbon atoms to the ring) with respect to the viscosity index. For oils with viscosity indices above 90 (although there is a marked scattering of points) there is some semblance of linearity between viscosity index and percentage of carbon atoms in naphthene rings.

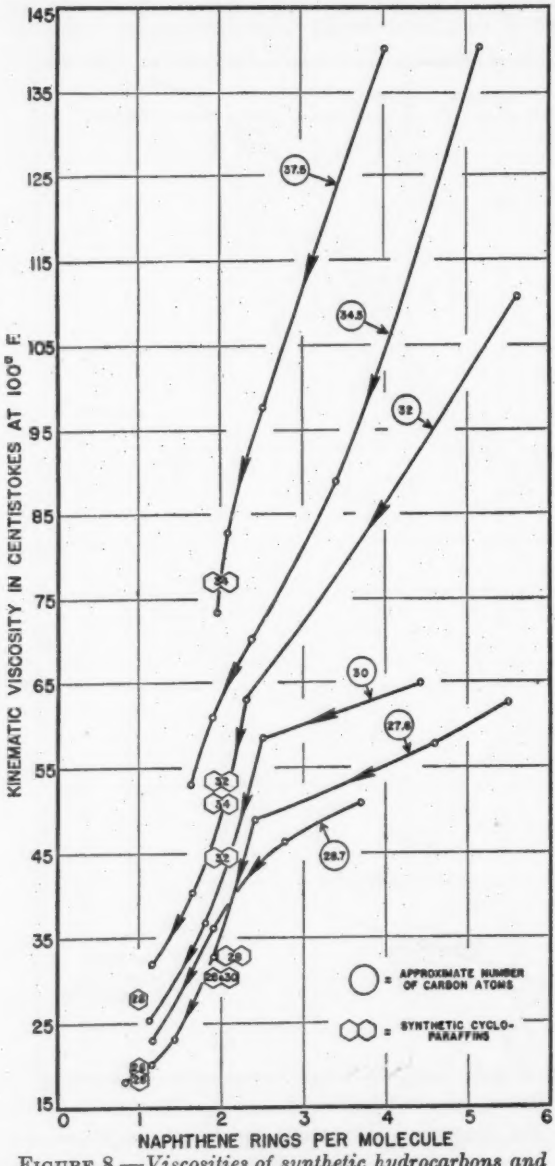


FIGURE 8.—*Viscosities of synthetic hydrocarbons and petroleum fractions.*

The majority of the fractions with viscosity indices below 90 (i.e., the first and second key fractions) are definitely out of line, their viscosity indices being much higher than would be expected if only naphthenes were present. This abnormality is undoubtedly due to aromatics or unsaturated material, the presence of which in these fractions is evidenced by the specific refraction, specific dispersion, and aniline points.

In the lower portion of figure 7 is shown a plot of the viscosity index with respect to the percentage of carbon atoms in naphthene rings for series *A*, together with those for a number of synthetic naphthenic hydrocarbons. The viscosity indices of the synthetic hydrocarbons show the effect of constitutive differences besides that of cyclization, but are in as good agreement with those of the fractions from petroleum as could be expected.

7. VISCOSITIES

In figure 8 are plotted the kinematic viscosities at 100° F of the key fractions from petroleum with respect to the number of rings they

contain. The fractions from each extraction charge are connected with arrows which indicate the order of their extraction. The approximate number of carbon atoms in each series is indicated by the figures shown in the circles. Also represented in the figure by hexagons are a number of synthetic naphthenes, the figures within the hexagons indicating the number of carbon atoms contained in each naphthene. As has been observed by other investigators, both increase in molecular weight and increase in the degree of cyclization of the petroleum fractions cause an increase in the viscosity. As with the other properties, and presumably for the same reason (i. e., the presence of aromatic and unsaturated hydrocarbons), the first key fractions show abnormal viscosities, which were lower than expected. The synthetic naphthenes show the effect of constitutive differences

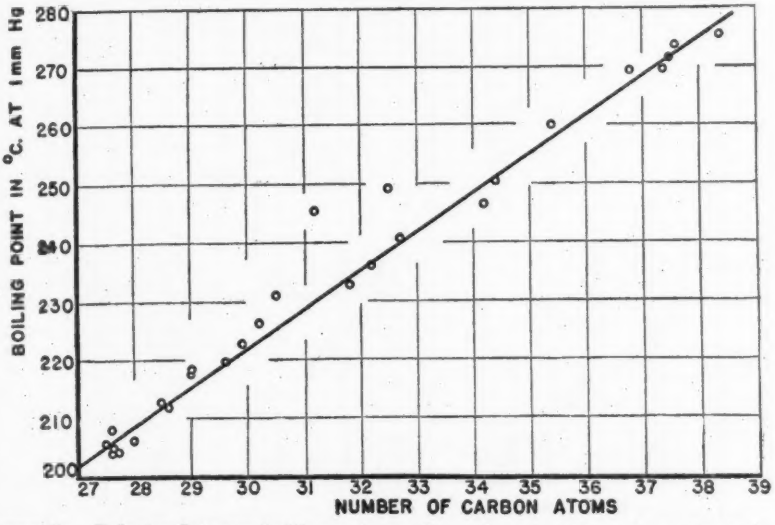


FIGURE 9.—*Relation between boiling point and number of carbon atoms of petroleum fractions.*

other than cyclization, but are in as good agreement with the fractions from petroleum as could be expected.

8. BOILING POINTS

In figure 9 are plotted the boiling points at 1 millimeter Hg pressure of the key fractions, with respect to the number of carbon atoms. A straight line represents the data fairly well, with the exception of two points.

As far as can be told from these data, the boiling point is a function of the number of carbon atoms and does not depend (at least to within about $\pm 3°$ C) on the number of naphthene rings in the molecule.

V. EXAMINATION OF THE PROPERTIES OF THE FRACTIONS FROM SERIES *A*

In this discussion of physical properties and constitution, so far only the key fractions, on which a large number of physical properties were determined, have been considered. It is now in order to con-

sider the properties of all the fractions from one charge. For this purpose the fractions from charge *A*, which was systematically extracted twice, will be considered. Charge *A* was divided into three equal parts (see fig. 1) and each part extracted separately. The resulting fractions were then blended according to their physical properties to make up three new charges, each of which was again extracted. In figures 10, 11, and 12 are plotted the refractive indices, viscosities, and viscosity indices of the fractions with respect to the percentage by weight of the charge for both the first and second extractions. The range in physical properties and total weight of the fractions which it was necessary to blend in preparation of the second set of charges are indicated at the right of the figures.

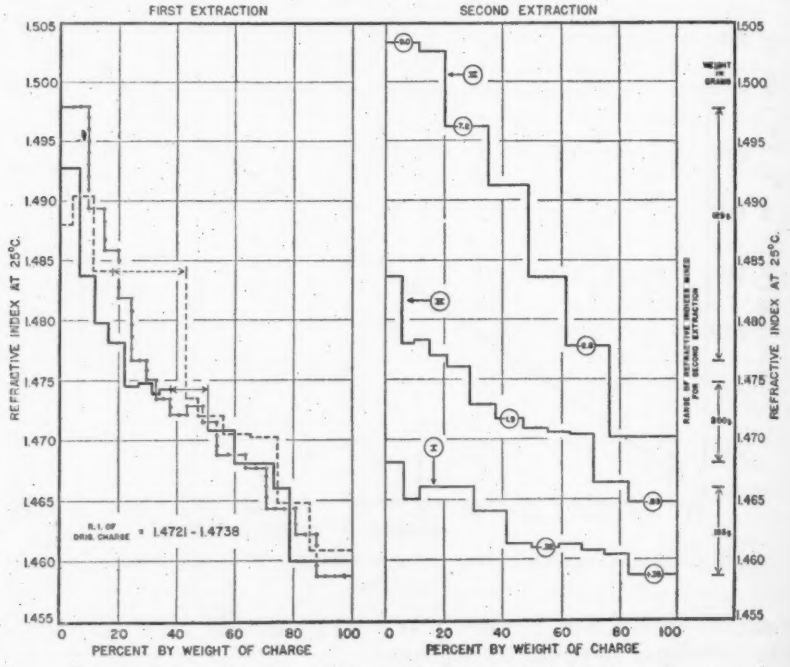


FIGURE 10.—*Refractive indices of fractions belonging to series A.*

The wide spread in the properties of the fractions from the first extraction is evident. The spread in properties of the fractions from each charge in the second extraction is less, and in the case of the less soluble fractions is scarcely more than the spread in properties of the fractions which were blended to make up the charge. This indicates that the limit of separation, with acetone as a solvent, and with the small charges available, has about been reached. There is a suggestion from the constancy of physical properties indicated by the flat portion of curves *I* and *II* that compounds of one type are concentrating in these regions, particularly since the empirical formulas in these regions correspond approximately to monocyclic and dicyclic naphthenes. One of the most interesting features of curve *III* is the fact that the viscosity decreases for the first few fractions, then rises markedly; the viscosity index also shows a similar peculiarity increas-

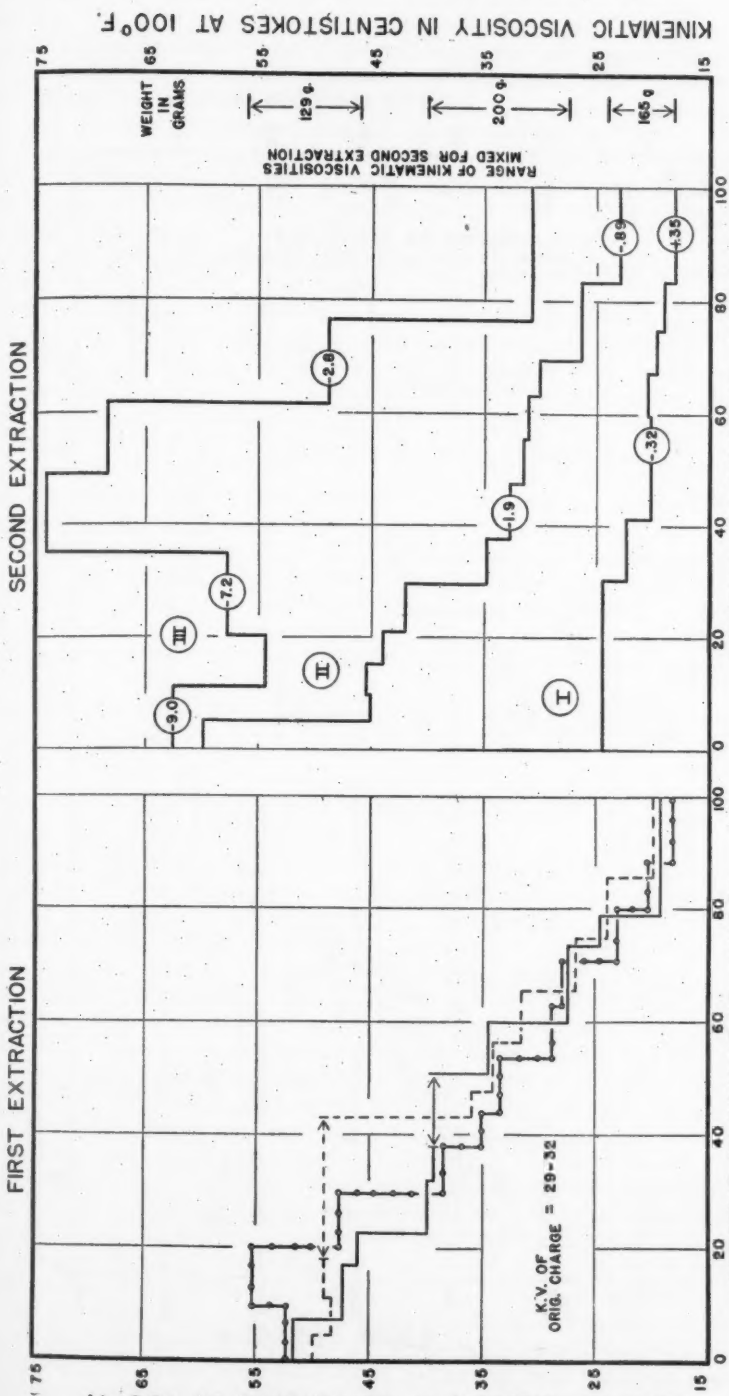


FIGURE 11.—*Viscosities of fractions belonging to series A.*

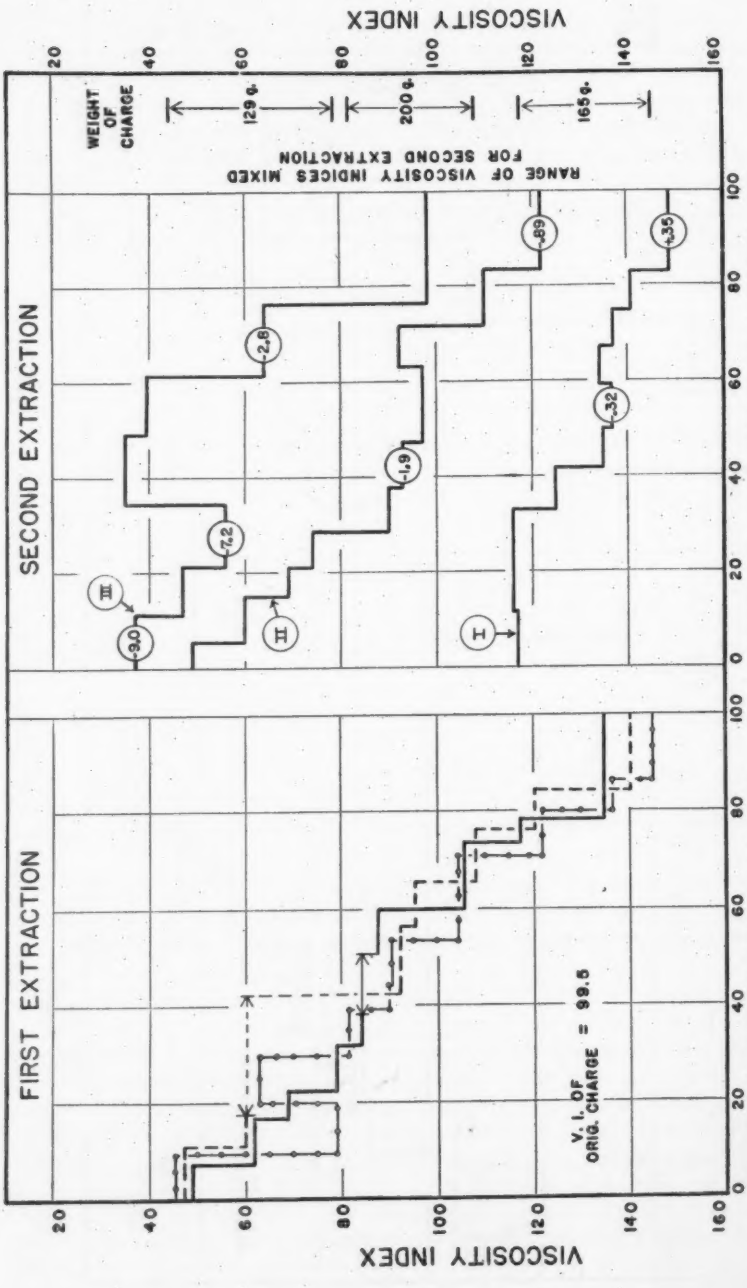


FIGURE 12.—*Viscosity indices of fractions belonging to series A.*

ing for the first few fractions, then decreasing markedly. These abnormal variations in viscosity and viscosity index are evidently not due to any change in the efficiency of the extracting column, since the refractive indices for these fractions decrease in a perfectly normal manner, but must instead be attributed to the fact that in this region we are dealing with a mixture of substances with markedly different viscosity characteristics. As has already been pointed out, the first fractions extracted contain small amounts of oxygen compounds, unsaturated material and probably aromatic hydrocarbons, and the abnormal viscosity characteristics are probably attributable to one or all of these substances.

Mikeska [1] has shown, from his study of the properties of synthetic compounds, that unsaturation does not appreciably change the viscosity characteristics. Therefore, if the unsaturated compounds in the first few fractions have the same composition (except for unsaturation) as the naphthenes contained in these fractions, then no abnormalities in viscosity would be expected. However, it is probable that the unsaturated material in these fractions is more nearly analogous in composition to the original charge, and consequently has a higher viscosity index and lower viscosity than the naphthenes in the fractions with which it occurs. This might account for the comparatively high viscosity indices and low viscosities of the first few fractions. The possibility that these anomalies are caused by aromatic hydrocarbons with high viscosity indices raises some interesting speculations which are considered in the succeeding paragraph.

VI. SPECULATION CONCERNING THE TEMPERATURE COEFFICIENT OF VISCOSITY OF THE AROMATIC EXTRACTS

Mikeska [1] has shown that in changing from a naphthene ring to an aromatic ring, without altering the rest of the molecule, there is some decrease in viscosity but no appreciable change in the viscosity index, and that aromatic hydrocarbons with one or two rings attached to long paraffin side-chains have, like the corresponding naphthenes, remarkably high viscosity indices. One might then naturally expect some material of high viscosity index in the supposedly aromatic extracts from petroleum. Yet to date no extract material of high viscosity index appears to have been found. Whether this material does not exist in petroleum, or whether its presence has been overlooked, is an interesting question. In figure 13 (curve *I*) are plotted the viscosity indices with respect to the number of rings in the molecule of the key fractions resulting from the double extraction to which reference has already been made. The 5 key fractions which contain no aromatics form a smooth curve which has been extrapolated to indicate (this requires experimental verification) what would be the viscosity index of a naphthene with 6 rings and 28 carbon atoms. On the basis of Mikeska's conclusions just referred to, curve *II* has been constructed identical in shape with curve *I* and indicates what would be the viscosity indices of aromatics analogous in constitution to the naphthenes of curve *I*. Curve *II* is displaced from curve *I* in such a manner that monocyclic aromatics fall above hexacyclic naphthenes. If aromatics with one ring have solubilities not far removed from those naphthenes with six rings (as was indicated to be probable in the discussion of aniline points on p. 932), it is easy to see why aromatic

extracts of high viscosity index have not been obtained. In the modern methods fractions with wide boiling ranges are extracted, and the mononuclear aromatics of high viscosity index would always be mixed with polynuclear naphthenes of low viscosity index. This question, in addition to its theoretical interest, is of considerable practical importance, since the petroleum industry today may be discarding, in the solvent extraction processes, aromatic material with

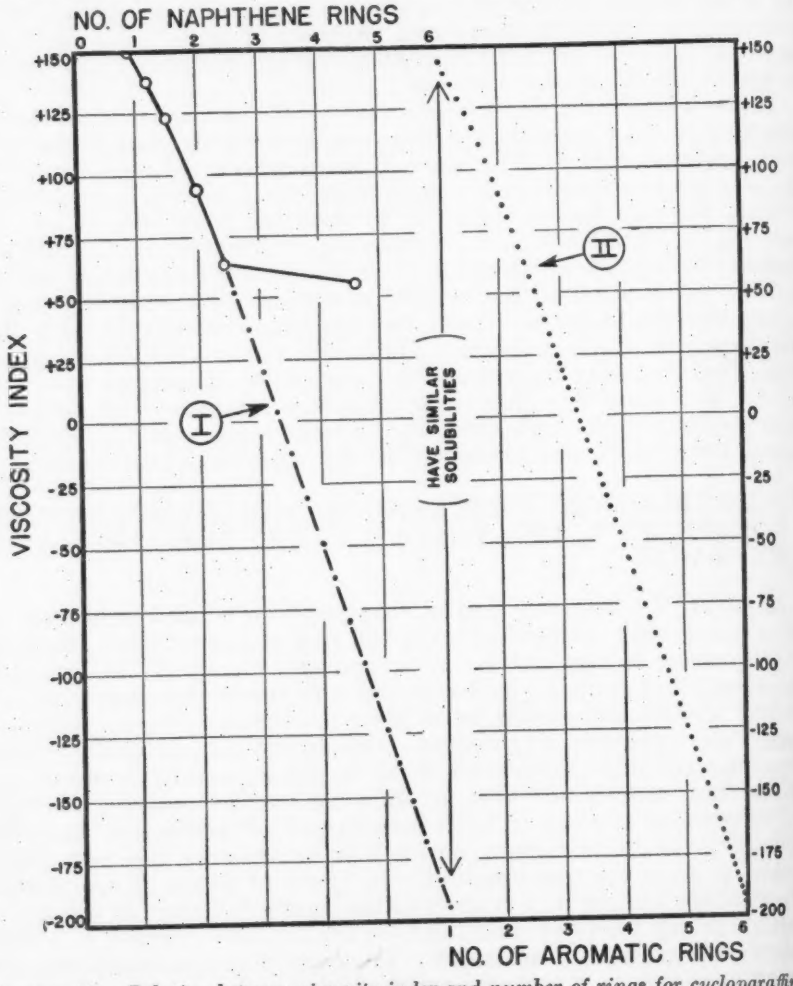

NO. OF NAPHTHENE RINGS
0 1 2 3 4 5 6
+150 +125 +100 +75 +50 +25 0 -25 -50 -75 -100 -125 -150 -175 -200
VISCOSITY INDEX
I
II
HAVE SIMILAR SOLUBILITIES
1 2 3 4 5 6
NO. OF AROMATIC RINGS

FIGURE 13.—*Relation between viscosity index and number of rings for cycloparaffins and for aromatic hydrocarbons.*

viscosity characteristics as good as the best naphthenic material and with oxidation characteristics which may be as desirable.

VII. THE QUESTION OF THE PRESENCE OF ISO- OR BRANCHED-CHAIN PARAFFINS IN LUBRICATING OIL

Whether iso- or branched-chain paraffins are an important constituent of mineral oils is a question concerning which there have been differences of opinion. Kyropoulos [15] came to the conclusion, as a

result of comparing the refractive indices and densities of fractions of a Pennsylvania oil with those of synthetic hydrocarbons, that it was composed largely of isoparaffins. Vlugter, Waterman, and Van Westen, considering the same data on the same oils, show that the specific refractions are too low to be accounted for on the assumption of the presence of isoparaffins, and concluded that these oils are composed of naphthenes. An examination of the literature shows that of the many fractions of wax-free lubricating oils from a wide variety of sources, and prepared by widely different methods, none have been found with a positive value of x in the formula C_nH_{2n+x}. An examination of the key fractions used in this investigation shows only one fraction with a positive value for x ($x=+0.35$) in the formula C_nH_{2n+x}. This fraction contained a small amount of wax, which was removed and identified from its melting point and refractive index as being composed of normal paraffin hydrocarbons. Negative values for x do not, however, prove the absence of isoparaffins, since mixtures of a dicyclic naphthene with an isoparaffin may give negative values for x. Nevertheless, the fact that there were observed no fractions richer in hydrogen than C_nH_{2n}, (except for that one known to contain normal paraffins) obtained from an extraction process which was definitely separating the oil into fractions containing respectively more or fewer naphthene rings, and which should consequently have separated isoparaffins, is considered strong evidence that no appreciable percentage of isoparaffins exists in these fractions.

Indeed, even the supposed existence of isoparaffins in wax from petroleum needs reexamination, since the determination of the empirical formulas of some waxes in this laboratory [16] has shown that certain waxes melting some 35° C below the corresponding normal paraffins, and which formerly were supposed to consist of isoparaffins, show considerable deficiencies in hydrogen from the formula C_nH_{2n+2}.

VIII. CONCLUSION

From the comparisons and analyses which have been made in the preceding pages, the following conclusions may be drawn.

1. The least soluble portion of the oil—that is, the material corresponding to the most highly refined product obtained by any good solvent-extraction process, consists substantially of naphthenes (cycloparaffins) containing from one to about three rings to the molecule together with the necessary alkyl radicals. The somewhat more soluble portion consists of naphthenes with more rings, together with some unsaturated hydrocarbons and possibly some aromatic hydrocarbons.

2. There is no evidence whatever for the existence of iso- or branched-chain paraffins in the lubricating oil from midcontinent crude.

3. Because of the similar solubility relations, it is possible that, in the extraction processes as used at the present time one-ring aromatic hydrocarbons are being discarded to waste along with the undesirable naphthenes containing about six rings to the molecule. This is a point well worth investigating, since these one-ring aromatic hydrocarbons may be a valuable constituent for good lubricating oil.

The authors express their gratitude for the advice and encouragement of F. D. Rossini. They wish also to thank L. A. Mikeska, of the Standard Oil Development Company of New Jersey, for transmitting to them prior to publication his very interesting manuscript on synthetic hydrocarbons of high molecular weight.

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WASHINGTON, September 2, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP955

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ISOLATION OF AN ISONONANE FROM PETROLEUM—ITS FRACTIONATION FROM NAPHTHENES BY DISTILLATION WITH ACETIC ACID [1]

By Joseph D. White [2] and Frank W. Rose, Jr.[2]

ABSTRACT

A nonane boiling at 135.2° C, probably a dimethylheptane, has been isolated from Oklahoma petroleum. It was found closely associated with naphthenic hydrocarbons in a distillation fraction boiling normally between 135 and 136° C from which aromatic hydrocarbons had already been removed. Separation of the mixture by distillation with glacial acetic acid yielded a fraction highly concentrated in the nonane from which the compound was finally isolated by crystallization from solution in liquid dichlorodifluoromethane. It constitutes about 0.1 percent of the crude petroleum.

The physical constants of the nonane have been determined and compared with those of nonanes known to boil near 135° C. It has properties similar to those of 2, 6-dimethylheptane, but the agreement is not sufficient, in the absence of knowledge concerning other possible isomers, to identify the compound completely.

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I. INTRODUCTION

In the first systematic examination of American petroleum, Pelouse and Cahours [1][3] obtained, upon treating a distillate "boiling within close limits" with concentrated sulphuric acid and redistilling the residual oil, a fraction which boiled between 136 and 138° C. On the basis of its vapor density they called the material *hydrure de nonyle*. It was characterized by them as having an odor faintly like that of lemons. Twenty years later, Lemoine [2], in a similar investigation obtained a fraction boiling within the range 135 to 137° C, which he designated as α-nonane. The exact source of the petroleum used in

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum. This paper was presented before the American Chemical Society meeting in Pittsburgh, September 1936.

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[3] Figures in brackets throughout the text indicate references listed at the end of the paper.

each investigation was not recorded. Most likely it came from eastern Canada or from the Appalachian fields. On the other hand, contemporaneously with Pelouse and Cahours, Warren, in a more carefully conducted examination of Pennsylvania petroleum, found no nonane which boiled near 135° C [3]. No other investigation of the composition of petroleum has revealed the presence of such a nonane.

Neither of the nonane fractions obtained by the above investigators closely resembled a pure aliphatic hydrocarbon in physical properties. This is not at all surprising since the nonane, whose separation from a midcontinent petroleum is described below, was found mixed with a naphthene hydrocarbon in an approximately constant-boiling distillate. An exhaustive distillation did not separate the nonane completely and only by subsequent crystallization could the compound be isolated in a nearly pure state.

II. PRELIMINARY DISTILLATION

In the course of separating the hydrocarbon constituents in an Oklahoma petroleum,[4] a 35-liter fraction was obtained which distilled between 130 and 140° C. After extracting the aromatic constituents [4], a redistillation of the residual oil at reduced pressure yielded a 9-liter fraction, boiling in the narrow range of 93 to 94° C at 215 mm (around 136° C at 760 mm), which was composed of a mixture of paraffin and naphthene hydrocarbons. Its refractive index [5] of 1.418, when compared with those for paraffin and naphthene hydrocarbons boiling near 136° C (1.400 and 1.430, respectively) showed that it was somewhat enriched in the naphthene constituents. In an effort to resolve the fraction into its components, it was again systematically distilled—this time at atmospheric pressure and through more efficient columns packed with brass locket chain. With a reflux ratio of approximately 15:1, the distillation proceeded at a rate of 0.5 to 1 ml a minute. The distillate was collected in 50-ml cuts which were sorted and combined according to boiling point and refractive index and redistilled in the same manner.

To guard against decomposition of the material at its elevated temperature of boiling, the distillation was carried out in the presence of carbon dioxide. Even so, the still residues, in which the naphthene was concentrated, were partially decomposed when distillation was carried too far. To minimize this, a large portion of a charge—frequently a third—was generally left undistilled.[6]

At the end of four distillations, the fractionation had proceeded as far as was feasible. Figure 1 shows the relation of the volume and refractive index of the resulting distillate to its boiling range. The lower step-wise line indicates the volumes of combined fractions which boiled within half-degree ranges. The upper line represents their refractive indices. The smooth curve imposed upon the upper line represents, without indicating the individual points, the refractive indices plotted against the boiling points of the 50-ml distillation cuts before pouring them together. The marked slope of the curve, as

[4] A description of the oil is given in BS J. Research **2**, 469, table 1 (1929) RP45, and in J. Research NBS **15**, 212 (1935) RP824.

[5] All refractive indices in this paper are for n_D^{25}, unless otherwise noted.

[6] Redistillation of the combined naphthenic residues resulted in pronounced decomposition, as evidenced by the brown color and unpleasant pungent odor of the still residue. If, however, the residues were first filtered through a small amount of silica gel, the colored and odorous material could be adsorbed and the filtered oil largely stabilized towards decomposition upon subsequent distillation.

well as its minimum for material boiling near 135° C., indicates that the distillation had partially separated the original mixture into its component hydrocarbons. Comparing the volumes of distillate with the refractive indices reveals that a fraction, more paraffinic than the others, was obtained which boiled between 135 and 135.5° C. A smaller and lower-boiling fraction obviously contained a naphthene, and a larger fraction, boiling higher, contained another naphthene as

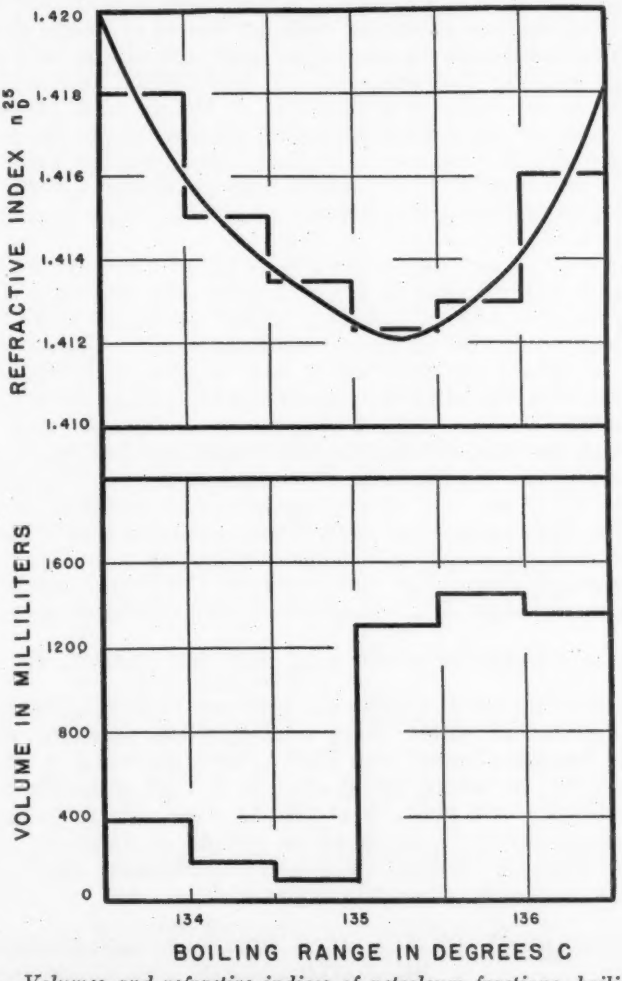

FIGURE 1.—*Volumes and refractive indices of petroleum fractions, boiling between 133.5 and 136.5° C, after being distilled through chain-packed columns.*
Lower graph, volume distribution; upper graph, refractive indices; upper curve, change in refractive index with boiling point.

its chief constituent. The isolation from this petroleum of the two naphthenes, ethylcyclohexane and a nonanaphthene, has already been reported [5].

The paraffinic fraction ($n=1.4123$) still contained a large amount of naphthene. While it could be crystallized from solution in liquid propane and methane, it could not be fractionated by crystallization, probably because it was nearly eutectic in compostion.

III. CONCENTRATION OF THE PARAFFINIC CONSTITUENT BY DISTILLATION WITH ACETIC ACID

1. METHOD

A relatively large fraction, composed chiefly of the paraffin constituent, was obtained by redistilling the material with glacial acetic acid. S. T. Schicktanz [6], while working in this laboratory on a similar problem with a petroleum fraction boiling near 165° C, found that, by distilling the oil mixed with an excess of acetic acid, all of it could be distilled out as azeotropic mixtures of the acid with the constituent paraffin and naphthene hydrocarbons, leaving a residue of the acid in the still. Fractionation of the oil took place because of a difference in the boiling points of the azeotropic mixtures. At his suggestion, a portion of our material was distilled with the acid, with the result that a most satisfactory separation of the paraffin from the higher-boiling naphthene occurred. The procedure was as follows:

A mixture of 1 liter of oil (bp=136 to 136.5° C; n=1.4160) and 1.5 liters of acid was distilled in a 3-liter glass still, having a column of 30 plates equipped with bubbling caps. A reflux ratio of about 20:1 and a rate of 35 ml an hour were maintained. The distillate was collected in 100-ml fractions which were shaken with 400 to 500 ml of water to separate the oil from the acid. After drawing off the acid layer, the oil was washed acid-free with further small portions of water and analyzed by its refractive index and boiling point.

In the test case, the fractions of washed distillate ranged in boiling point from 135.5 to 137° C and in refractive index from 1.408 to 1.427. The wide range in refractive index showed that a pronounced separation had taken place. Using the procedure outlined, the 4.2 liters—shown in figure 1 to boil between 134.5 and 136.5° C—was accordingly subjected to a systematic distillation with acetic acid.

2. CHARACTERISTICS OF THE DISTILLATION

All fractions distilled, except the first one or two which contained a small amount of water, were homogeneous solutions at 25° C. The initial fractions boiled near 109° C, were enriched in the paraffin constituent and contained 50 ml of oil in 100 ml of distillate. Those distilling near the end boiled near 110° C, were rich in the naphthene, and contained about 47 ml of oil in 100 ml of distillate. The last fraction to contain oil held only a few milliliters, which consisted chiefly of aromatic constitutents (xylenes).[7]

3. COMPARISON OF THE ACID DISTILLATION WITH THE OIL DISTILLATION

In order to point out more clearly the effectiveness of the acid distillation in separating the paraffin-naphthene mixture, the results of distilling certain fractions of the oil through columns packed with

[7] This discovery led to our developing a method, which we expect to publish later, for separating the aromatic from aliphatic and naphthenic hydrocarbons in the petroleum fraction boiling between 155 and 160° C. A solution of isopropylbenzene (boiling point 153.5° C) and acetic acid was found to distil several degrees higher than the azeotropic mixtures of the acid with the paraffins and naphthenes boiling near 155° C. Similar facts account for the ease with which the xylene constituents are separated from a mixture of petroleum hydrocarbons boiling near 136° C when it is distilled with acetic acid. Lecat found the boiling point of the azeotrope of acetic acid-*m*-xylene to be 115.38° C. See Int. Crit. Tables 3, 319 (McGraw-Hill Book Co., New York, N. Y., 1928.)

locket chain are compared in figure 2 with those obtained by distilling similar fractions with acetic acid, through columns equipped with bubble-cap plates. In the figure, the refractive indices of selected

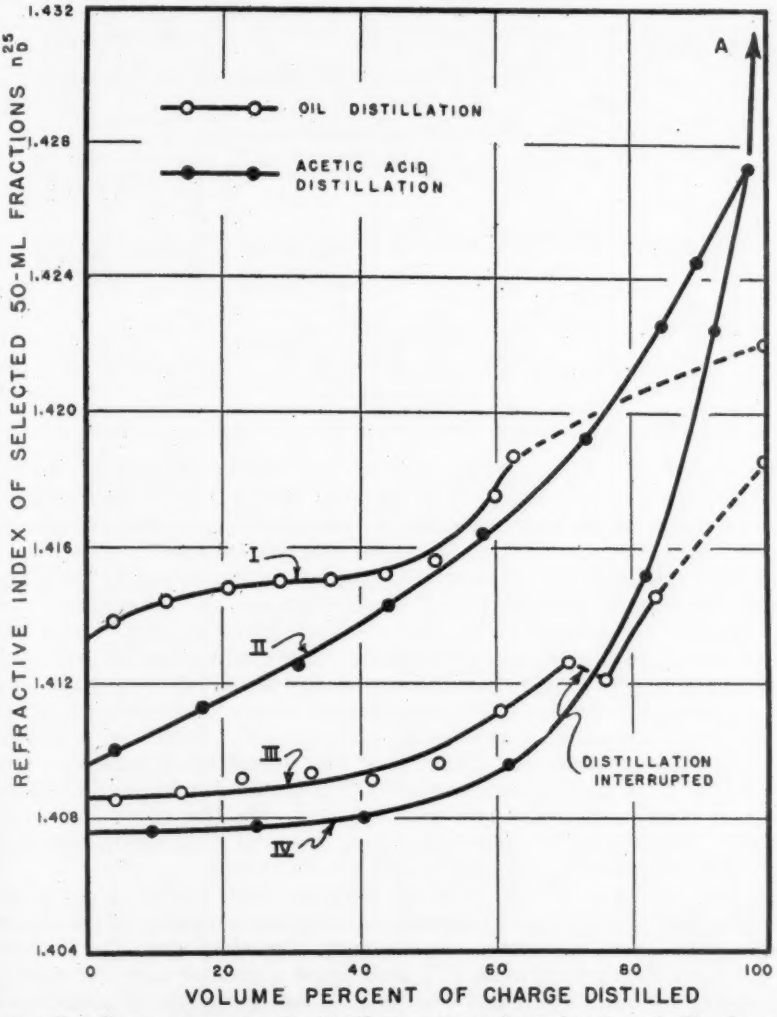

FIGURE 2.—*Curves comparing the distillation of petroleum fractions, boiling between 135.5 and 136.5* C *alone and with glacial acetic acid*

Curves *I* and *II* show the progressive change in composition (refractive index) of the distillate during distillation of material enriched in naphthene. Curves *III* and *IV* show the same for material enriched in paraffin. For properties of the material distilled, see table 1.

50-ml fractions of distilled oil are plotted against the percentage of the original charge distilled. The properties of the material used, and the conditions under which its distillation was carried out, are given in table 1.

TABLE 1.—*Properties of the oil, and distillation conditions used to obtain the curves shown in figure 2*

Curve	Type of distillation	Oil used for distillation				Type of column used	Total amount of distillate per hr[1]
		Boiling range	Refractive index, n_D^{25}	Amount	Source		
		°C		ml			ml
I	Oil	136.0 to 136.5	1.418	1,320	Oil distillation	Glass column, 2.5 m tall, chain-packed; 60 theoretical plates; hold-up, 160 ml.	46
II	Oil with acetic acid.	136.0 to 136.5	1.4175	1,200	Equal parts from oil distillation and acid distillation.	Glass column, 2.5 m tall, 30 bubble-cap plates; 25 theoretical plates; hold-up, 160 ml.	36
III	Oil	135.5 to 136.0	1.412	1,100	Acid distillation	Same as for curve *I*	20.5
IV	Oil with acetic acid.	135.5 to 136.0	1.4125	990	Oil distillation	Same as for curve *II*	35

[1] A reflux ratio of 15:1 was maintained for the oil distillations; 20:1 for the acid distillations.

Curves *I* and *II* of figure 2 show the results of each of the two methods in distilling material containing about 2 parts of naphthene to 1 part of paraffin hydrocarbons. The curves have the same general shape, but the wide range in refractive index shown in curve *II* indicates that a better separation resulted from the acid distillation. Since the column in which the oil distillation was carried out had much the greater efficiency rating, the results obtained with it can only mean that the material is difficult to separate when distilled as oil. Conversely, in the acid distillation, the pronounced separation must have resulted from the better distillation conditions arising from the presence of the added component, and, notably, from the azeotropic relations of the mixture. Because of the necessity of leaving a large residue from the oil distillations, no comparison can be made between the end fractions of the two distillations. On the other hand, it is obvious that the initial fractions from the acid distillation contained a greater concentration of the paraffin constituent.

Curves *III* and *IV* show that likewise with material containing the paraffinic compound as the major constituent, the acid distillation yielded the more paraffinic concentrate. In this case, the first half of the acid distillate (curve *IV*) contained a greater concentration of paraffinic material than did the first 50 ml from the oil distillation.

In addition to effecting a better separation of the naphthene and paraffin constituents, the distillation with acetic acid had the advantage of permitting smaller initial quantities of oil to be distilled without leaving a residue of oil. This permitted the systematic distillation to be carried well towards completion. A further advantage was the readiness with which any aromatic material present could be separated from the other classes of hydrocarbons. This is illustrated in curve *IV* of figure 2 by the arrow and the letter *A*, which represents the last 2.5 percent of distillate. The average refractive index for this small fraction was 1.450, which indicates that about a third of it was aromatic hydrocarbon. Finally, in the acid distilla-

tion, no thermal decomposition of the oil occurred as it did from prolonged heating of the still residues in the oil distillation.

The chief disadvantage of the acid distillation was the necessary washing of the distillate to free the oil from acid.

4. RESULTS OF THE ACID DISTILLATION

The results of systematically distilling the petroleum fraction with acetic acid are given in figure 3. The lines and curves have the same

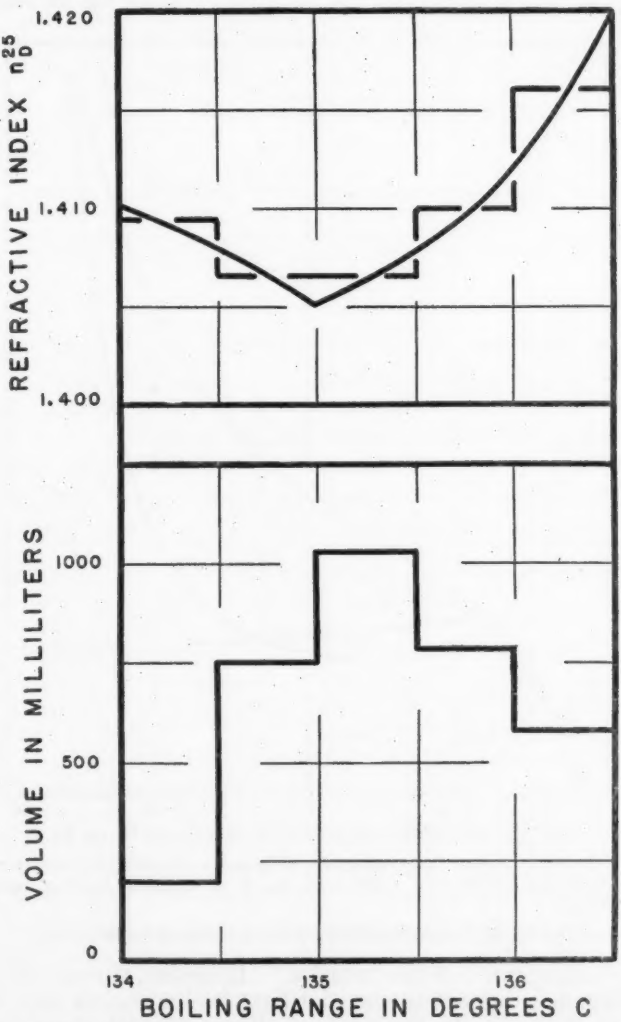

FIGURE 3.—*Volumes and refractive indices of petroleum fractions boiling between 134 and 136.5° C after distillation with acetic acid.*

The graphs and curve have the same significance as in figure 1.

significance as in figure 1. A liter of the nonanaphthene (bp=136.7°C) was removed, which left about 2.5 liters of paraffin concentrate boiling between 134.5 and 136.0° C. The largest single fraction boiled between 135 and 135.5° C, which indicated that the boiling point of the paraffin hydrocarbon lay within these limits.

Towards the end of the distillation, further concentration of the paraffin constituent became slow, the separation being complicated by the presence of some ethylcyclohexane. In the refractive index curve of figure 3, it is observed that the distillate boiling at 135.0° C had the lowest value, 1.405, and therefore contained the least amount of naphthene. That some naphthene remained in this fraction was later verified from the refractive index, 1.399, of the pure paraffin. Probably as a result of the azeotropic conditions, a small amount of ethylcyclohexane persisted in the distillate boiling up to and slightly

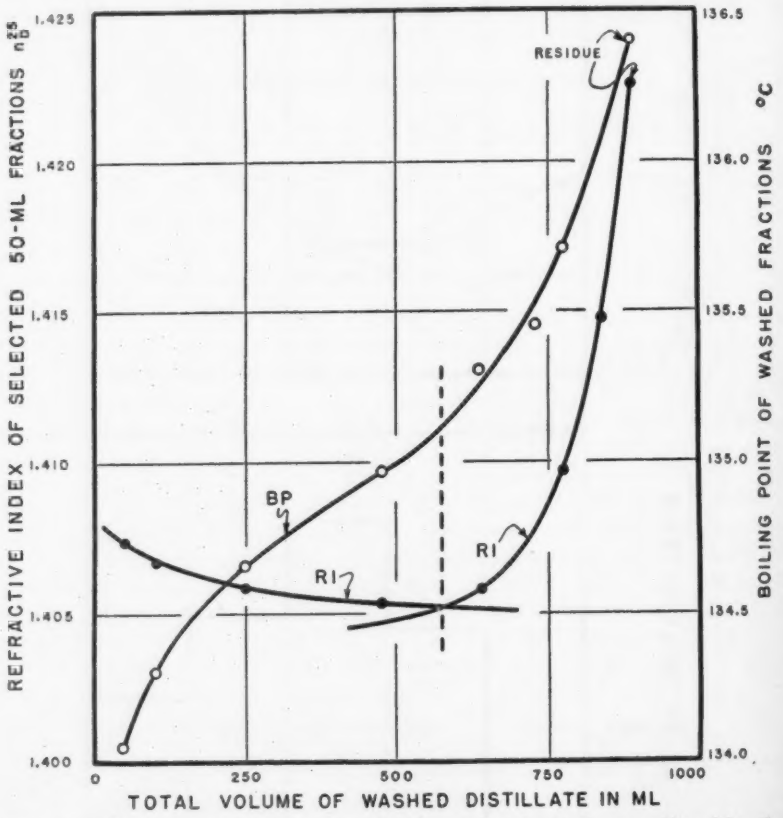

FIGURE 4.—*Curves showing the progressive change in physical properties of fractions resulting from the distillation with acetic acid of material boiling between 134.8 and 135.2°* C.

White circles represent boiling points; black circles, refractive indices.

above the boiling point of the paraffin.[8] Likewise, the nonanaphthene, in turn, began to appear in the distillate boiling below 135° C. The situation is illustrated by the curves in figure 4 which show the change in boiling point and refractive index of material boiling between 134.8 and 135.2° C when distilled with acetic acid. The minimum for the refractive-index curve seems to correspond with material boiling at 135.1° C.

[8] This was found to be the case when a redistillation of material boiling immediately above that temperature, and from which a portion of the paraffin had been removed by crystallization, yielded fractions containing ethylcyclohexane.

The inability to obtain a fraction of nearly pure paraffin hydrocarbon by distilling the material described above with acetic acid is explained in part by the data given in table 2, which show that the minimum boiling points of the constituent hydrocarbons with acetic acid are closer together than the boiling points of the constituents themselves.

TABLE 2.—*Boiling points of three hydrocarbons compared with the boiling points of their acetic acid azeotropes*

Hydrocarbon	Boiling point 760 mm	Azeotropic boiling point (approx.) 760 mm
	°C	°C
Ethylcyclohexane	131.8	107.9
Isononane	135.2	[a] 108.8
Nonanaphthene	136.7	109.6

[a] For a fraction of the nonane having boiling point = 135.5° C; n_D^{25}=1.4045. All other values in this table were obtained with the best samples of the hydrocarbons isolated from petroleum. See table 4 and reference [5].

Although distillation with acetic acid resulted in a decided separation of the petroleum fraction herein discussed, it is not to be concluded that every mixture consisting of paraffin and naphthene hydrocarbons, and boiling in a narrow temperature range, can be so separated. Mixtures of this kind exist in which the azeotropic relations cause both classes of hydrocarbons to distill at the same temperature with acetic acid.

IV. ISOLATION OF THE PARAFFIN CONSTITUENT BY CRYSTALLIZATION FROM SOLUTION

When various fractions of the paraffinic material obtained from the acid distillation were cooled they could not be induced to form crystals but they would suddenly become viscous at −115° C. The sudden change in viscosity[9] seemed to indicate that the oil was tending to crystallize at this temperature. When diluted with an equal volume of liquid dichlorodifluoromethane, all of the distillate boiling within the range 134.7 to 135.7° C and having a refractive index less than 1.408 crystallized readily and yielded, on fractionation of the partially frozen material, a solid phase in which the paraffin was more concentrated. Systematic crystallization of a liter of material, which boiled between 135.3 and 135.8° C and ranged in refractive index from 1.4055 to 1.409, finally produced a nearly pure sample of an isononane. The progress of the separation of the compound is outlined in table 3.

TABLE 3.—*Progress of the fractional crystallization of the paraffin concentrate*

Stage	Volume	Refractive index, uncorrected	Initial freezing point, uncorrected
	ml	n_{21}	°C
Start	1,000	1.4070	Glass at −115
1st	540	1.4054	−114
2d	270	1.4038	
3d	170	1.4013	−107
4th	102	1.4000	−103.8
5th	50	1.3990	−103.0

[9] More recently we have observed the same phenomenon with the petroleum fraction boiling near 143° C, which contains the methyloctanes.

V. PROPERTIES OF THE ISONONANE

The 50-ml sample obtained after five crystallizations was refluxed over sodium to remove traces of solvent and then distilled. The time-temperature cooling curve of the distillate is recorded in figure 5. The curve shows that the sample had a freezing range of only 0.25° C, which indicates that the material, while not of the highest purity, was composed almost entirely of a single substance. Its nearly pure state was also indicated by the difference between its boiling point and condensation point. The small interval of 0.033° C was measured by M. Wojciechowski in a Swietoslawski ebulliometer of standard dimensions [7]. Further information concerning the sample's composition was obtained by determining its carbon-hydrogen ratio. From two determinations, the average ratio, moles H_2O/moles CO_2, was found to be 1.1082 ± 0.0004. (The experimental values were, respectively, 1.1086 and 1.1078.) Compared with the calculated value, 1.1111 for a nonane C_9H_{20}, and 1.0000 for a naphthene C_nH_{2n}, the value found

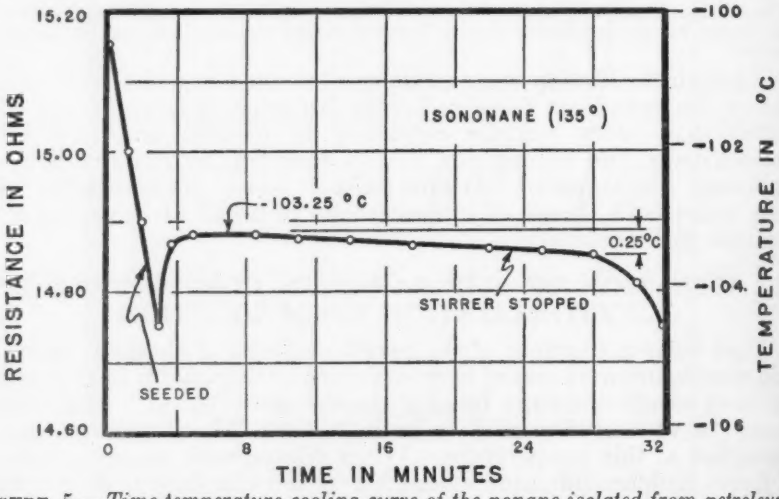

FIGURE 5.—*Time-temperature cooling curve of the nonane isolated from petroleum.*

indicated that the sample contained over 97 mole percent of the nonane.

The compound was found by H. S. Isbell of the Polarimetry Section of this Bureau to be optically inactive. It is further characterized by a very pleasant odor, but, unlike the fraction obtained by Pelouse and Cahours many years ago, it scarcely smells like lemons.

The physical constants of the isolated sample are listed in table 4.

TABLE 4.—*Physical constants of the isononane from Oklahoma petroleum*

Normal boiling point, °C	135.21±0.02.[a]
Difference between boiling and condensation, °C	0.033.[a]
Freezing point, °C	−103.25±0.05.
Specific gravity, d_4^{20}	0.70963 ±0.00002.[b]
Temperature coefficient, $\Delta d/\Delta t$	−0.00079 (20 to 25° C).
Refractive index, n_D^{20}	1.40115 ±0.00005.
Temperature coefficient, $\Delta n/\Delta t$	−0.00049 (20 to 25° C).
Critical solution temperature in aniline, °C	81.2 ±0.5.[a]
Carbon-hydrogen composition, $\frac{\text{moles } H_2O}{\text{moles } CO_2}$	1.1082 ±0.0004.

[a] Determined in a Swietoslawski ebulliometer by M. Wojciechowski. For method, see reference [7.]
[b] Determined by the Division of Weights and Measures of this Bureau.
[c] Determined by Wilson Heuer.

VI. RELATION OF THE ISOLATED NONANE TO THOSE KNOWN TO BOIL NEAR 135° C

A comparison of properties of the nonane from petroleum with those for a certain few of the synthetic nonanes is made in table 5. The properties of the isolated compound are the nearest like those of 2,6-dimethylheptane prepared by Konowalow, but are noticeably different from the properties of the same compound synthesized by Escourrou. This discrepancy prevents an accurate identification of the nonane from petroleum. Possibly it is 2,6-dimethylheptane. On the other hand, it is possible that the prototype of the isolated nonane has not yet been synthesized. Sixteen of the 35 structurally isomeric nonanes have been made. Of these, only those listed in table 5 boil near 135° C. It is quite likely that a few of the 19 unknown nonanes, especially other dimethylheptanes or some of the trimethylhexanes, boil in this region. The nonane from petroleum may be one of these. It follows, however, from its optical inactivity that the compound either contains no asymmetric carbon atom or is the *dl* mixture of its optical isomers.

TABLE 5.—*Comparison of properties of the isolated nonane with those of certain known nonanes*

Nonane C_9H_{20}	Boiling point 760 mm	d_4^{20}	n_D^{20}
	°C		
From Oklahoma petroleum:			
White and Rose	135.21	0.7096	1.4011
From "American petroleum":			
Pelouse and Cahours, Compt. Rend. **56,** 505 (1863)	136 to 138	[a].737	
Lemoine, Bul. soc. chim., Paris (1) **41,** 164 (1884)	135 to 137	[a].736	
2,6-Dimethylheptane:			
Escourrou, Bul. soc. chim., France (4) **43,** 1112 (1928)	134 to 135 [a]	[a].714	[a]1.402
Konowalow, Chem. centra. **77** (II), 313 (1906)	134.5 to 135.5 [a]	[a].711	[a]1.4007
2,5-Dimethylheptane:			
Clarke and Beggs, J. Am. Chem. Soc. **34,** 54 (1912)	135.6 to 135.9	[b].7198	1.4045
Levene and Marker, J. Biol. Chem. **91,** 418 (1931)	135	[a].716	
Levene and Marker, J. Biol. Chem. **95,** 13 (1932)	134	[a].719	
Tuot, Compt. Rend. **197,** 1434 (1933)	134 [a]	[a].713	1.4033
2,4-Dimethylheptane:			
Clarke and Beggs, J. Am. Chem. Soc. **34,** 60 (1912)	133.3 [a]	[b].7158	[a]1.4040
Tuot, Compt. Rend. **197,** 1434 (1933)	130.5 [a]	[a].711	1.4023
3,3-Dimethylheptane:			
Noller, J. Am. Chem. Soc. **51,** 598 (1929)	137 to 138	.7304	1.4095

[a] Constants are reported values corrected to 760 mm or to 20° C. For $\Delta t_B/\Delta P$, see Int. Crit. Tables **3,** 246 (McGraw-Hill Book Co., New York, N. Y., 1928). $\Delta d/\Delta t = -0.0008$; $\Delta n/\Delta t = -0.0005$.
[b] Richards and Shipley, J. Am. Chem. Soc. **38,** 996 (1916).

VII. CONTENT OF THE ISONONANE IN THE PETROLEUM

All fractions from the acetic acid distillation which boiled between 133.5° and 136.5° C contained the isolated nonane. No other paraffin hydrocarbon was present in a detectable amount. Further fractionation of the distillate, by distillation and crystallization, yielded 2.5 liters of assorted fractions in which the nonane was the chief constituent. The fractions ranged in boiling point from 135.0° to 136.0° C and in refractive index from 1.400 to 1.410.

The amount of isononane in this material as estimated from the refractive index was approximately 1.8 liters. The total quantity originally present, counting losses, was more than 2 liters, which, based on an original 2,300 liters of crude, amounts to about 0.1 percent of the petroleum.

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WASHINGTON, August 29, 1936.

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SELECTION OF COLORS FOR SIGNAL LIGHTS[1]

By Harry J. McNicholas[2]

ABSTRACT

Various colored lights produced by combinations of a tungsten-filament lamp and commercially available colored-glass light filters were tested for efficiency and accuracy of identification in each of two six-color signal systems consisting, respectively, of red, orange-yellow, white, green, blue, and purple lights, and of red, orange, yellow, white, green, and blue lights . The tests were made by 38 normal observers on an outdoor range of 950 feet, for different weather conditions and signal intensities. Comparison between the two systems under prescribed service conditions showed that the use of purple with adequate lamp intensity is preferable to the use of both orange and yellow with red and white. Partial chromaticity tolerances and minimum lamp intensities have been determined for the six-color system containing purple.

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I. STATEMENT OF THE PROBLEM

The selection of colors for a system of signal lights is determined primarily by the number of colors required and the service conditions. Colors may be chosen with due consideration to some common defects in color vision, or for use only by normal observers. The lights may be seen as point sources or of sensible size; they may appear in association with other lights and on different backgrounds. Practical signal intensities and variable atmospheric conditions also enter into the choice of the colors. If but two or three colors constitute the system a wide range of service conditions may be met satisfactorily, and some preference for different possible colors accommodated; but as the number of colors required increases the choice becomes definitely restricted and the range of service conditions greatly reduced.

On American railroads suitable ranges of red, green, yellow, and sometimes white have been adopted for use by normal observers at

[1] This work was undertaken at the request, and with the financial support, of the Bureau of Aeronautics of the U. S. Navy Department, and publication has been approved by that Bureau.

[2] The author is greatly indebted to various staff members of the National Bureau of Standards and the Bureau of Aeronautics for their cooperation in the recording and reduction of the field observations. In particular, the advice and contributions of F. C. Breckenridge and R. S. Hunter are acknowledged and appreciation is extended to C. G. Malmberg for help in the preparation of this publication.

moderate signal intensities for long-distance work. For short distances additional signals are obtained by use of low-intensity blue and purple. The different colors of this system are thus of unequal importance and all six need not be mutually distinguishable under every condition of service. These circumstances determine to some degree what specific ranges of each color class may be employed for highest signal efficiency. Similarly, in the use of red, yellow, and green for street traffic control, the bluish-green glass selected is conditioned chiefly by the desirability of accommodating a fairly common abnormality in color vision (red-green deficiency).

The present investigation was undertaken to determine the best colors and their tolerances for a six-color signal system to be used at night, over distances up to approximately 1,500 feet. All colors enter the system on equal terms and positive identification of each color is required by normal observers, without benefit of simultaneous contrast with one or more of the other five, and under atmospheric conditions varying from clear to light haze. The choice of colors is limited, furthermore, by practical considerations, to that range obtainable by combinations of an incandescent lamp, operating at a fixed color temperature, with commercially available and reproducible colored-glass light filters, in the form of globular or tubular cover glasses for the bare lamps. The signals must be identified when seen as point sources of moderate or low intensity, which may approach under most adverse conditions the limit of chromatic visibility for normal observers.

The most obvious selection of colors includes suitable ranges of red, yellow, white, green, blue, and purple. At the beginning of this investigation there was considerable uncertainty, however, as to the suitability of purple for the present purpose, and it was desirable to investigate thoroughly the possibility of the substitution of another color in its place. The objection to the purple signal arises from the following considerations: (1) A light source of relatively high candlepower is required for a given signal intensity to counterbalance the high absorption of light in all suitable purple glasses; (2) its identification as a point source depends almost entirely on the recognition of a dichromatic red-blue hue pattern which varies markedly from one observer to another; (3) it is susceptible to change toward the red by excess scattering of the blue component in hazy atmosphere.

The two most likely possibilities for the elimination of purple are (1) the insertion of orange and yellow between red and white, and (2) the use of a blue-green and yellow-green between blue and yellowish-white. It will be shown, however, that the latter suggestion is not feasible, so that the final choice is reduced to only two six-color sets of signal lights which will be denoted herein as sets *P* and *O* (purple and orange), respectively. Set *P* consists of suitable ranges of red, orange-yellow, white, green, blue, and purple; set *O* includes red, orange, yellow, white, green, and blue.

The specific purposes of the present investigation have been (1) to determine the maximum permissible chromaticity ranges for each color in the two six-color sets, (2) to indicate approximately the minimum lamp intensities (candlepowers) required for positive identification of each signal color, and (3) to make a direct comparison of the accuracy of identification of colors in the two signal systems. It is beyond the scope of the present paper to translate the selected chro-

maticity ranges and minimum signal intensities into corresponding tolerances in the transmissive properties of various light filters and in the color temperature and candlepower of the incandescent lamps. Inasmuch as only commercially available colored-glass filters were used in this investigation, the translation will always be possible for the establishment of practical purchase specifications for the lamps and colored glassware.

II. APPARATUS AND METHOD

1. LIGHT SOURCE AND TEST RANGE

For the production of suitable colored-light signals, apparatus is required by which the lamp-and-filter combination may be conveniently varied by successive interchange of different filters, and the signal or source intensity adjusted in each case to a prescribed value. The arrangement used is shown in figure 1. A 400-watt lamp was

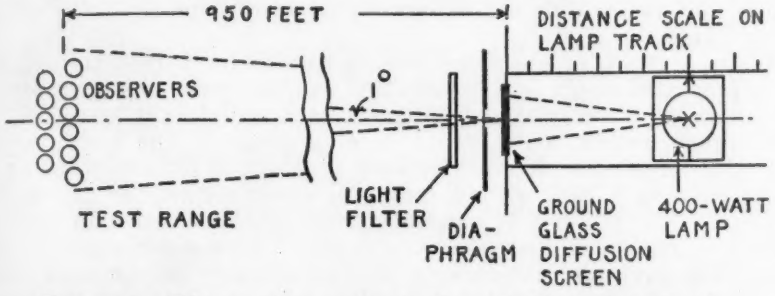

FIGURE 1.—*Diagram of apparatus for the production of light signals.*

operated at a color temperature of 2,840° K and mounted so that the distance from the plane of its filaments to the illuminated surface of a ground-glass diffusion screen could be varied at will. The diffusion screen was a plate of colorless borosilicate-crown glass, fine-ground on both sides, which served effectively as the source of light as seen by a group of observers stationed approximately 950 feet from the screen. The observers were grouped closely about the line of motion of the lamp filaments and subtended a horizontal plane angle of less than 1° at the source. The area of the diffusion-screen source was limited by one of a set of diaphragms with circular apertures ranging from 3 to 30 mm in diameter. Any one of these apertures could be centered in the line of sight of the observers and was placed close to the transmitting surface of the diffusion screen. Various filters could be inserted successively between the observers and the diaphragm.

The color of the signal was changed by the insertion of different filters; the signal intensity was controlled by proper choice of the diaphragm and the position of the lamp on the track. By means of an illuminometer mounted at a distance of 50 cm from the diffusion screen, with its test plate centered in the observers' line of sight, the candlepower of the source (without filter) was determined for the various diaphragms and lamp positions. Since the luminous transmission of each filter used was known, the proper diaphragm and lamp position could be chosen for each filter so that all signals could be shown at constant intensity if desired.

The test range extended from the flat roof of one building to that of another, both located on the grounds of the National Bureau of Standards. The apparatus described above was enclosed in a small roofhouse and the signals were exhibited through a diaphragmed hole in its wall. All observations were made in the early evening after dark. Observers were seated comfortably in the open and shielded from extraneous city lights. The signals appeared just below the horizon on a dark background of woodland and southern sky. Each observer was supplied with a board for support of his record paper. A low-intensity lamp with push-button switch was mounted conveniently on each board and could be lighted when needed for recording observations. Continuous telephonic communication was maintained between the observers and operators at the signal-sending station.

2. TEST METHOD

The field observations were necessarily divided into a number of separate test runs, each run being made with a selected set of test colors and under different observational conditions as described in section III.

When a group of observers was assembled for a run, the signals were presented singly in a prearranged random order unknown to the observers, who were asked to identify each signal as it appeared, as red, orange, yellow, white, green, blue, or purple. The first letter of the color name was recorded by each observer in definite order on a prepared record form without any oral announcement of the classification. The number of permitted classifications varied in accordance with the specific purposes of the test. An x was recorded if the signal was invisible; otherwise a definite decision on the color class was required. In some runs all colors were exhibited at the same signal intensity (series 1, table 3); in other runs two or three fixed source intensities were used with each filter (series 2, tables 4 and 5). In any run all different signals and all intensities of the same signal always appeared in random order. The complete single exhibition of all colors at all selected signal intensities was repeated many times, each time with a different random order of presentation, until each color had been shown a prescribed number of times, which varied from 2 to 15 in different runs.

The entire run was sometimes repeated under different weather conditions, signal intensities, or observer groups. Each signal lasted approximately 5 seconds, with about the same dark interval between the signals, during which the observers recorded their classification. Rest periods were provided as required.

Two operators were engaged in the presentation of the signals, one to interchange the filters and diaphragms, and the other to set the lamp in proper position and to supervise the course of the experiment in accordance with a master schedule of operations prearranged for the run. This schedule contained the actual order of presentation and prescribed intensities for the signals. The run was started, stopped, or irregularities corrected by telephonic communication between the operators and one observer, who was in charge of the test. After completion of the run the master schedule was compared with the record form of each observer and the individual color classifications were rearranged in definite order with respect to the test colors presented, the permitted classifications, and the source or signal intensities.

III. DESCRIPTION OF TEST COLORS AND OBSERVERS

A description of the signal colors as actually perceived is complicated by many complex factors. It is known that the perception of colors and the discrimination between them varies with the intensity and area of retinal illumination, and these factors become of considerable importance as the observational conditions approach the threshold of chromatic visibility for the very small sources with which we are herein concerned. Aberrations in the lens system of the eye also play an important role in the appearance and identification of the signals. For the average observer the greens, blues, and purples appear to spread over the field of view to a far greater extent than do the reds or yellows. The differential effect may be appreciable even between the adjacent red, orange, and yellow signals so that the apparent sizes of the "point" sources is of some assistance in the discrimination between them.

Purple filters transmit only the ends (red and blue) of the visible spectrum. For the majority of observers the identification of purple depends largely on the effect of chromatic aberration in the eye, resulting in a partial or complete spatial resolution of the purple into its red and blue components. Most normal observers see the purple source as a distinct red center surrounded by a diffuse blue halo or blue radial streamers. Some observers see this color pattern reversed. Others see the blue spread with the red concentrated along a horizontal line. Various other patterns and degrees of spatial resolution are observed, including cases wherein the dichromatic effect is indistinct so that the signal appears as nearly a true monochromatic purple spread. This partial resolution of a point source into chromatic components is also noted by a few observers for signal white. A poorly defined orange-yellow center may be seen surrounded by a greenish-blue spread. Such sources, at medium intensities, have been mistaken occasionally for green or purple in these tests.

The phenomena described all enter into the experimental selection of the signal lights, and complicate their precise description or specification. Little work has been done on the colorimetry of point sources, and established colorimetric methods are all referred to simplified conditions of observation which include retinal illuminations of 100 photons or above, with field sizes of 2° or more. Under these conditions the aberration effects are absent, large variations in intensity are of reduced importance, and definite experimental relations are established for purposes of practical colorimetry. In general, the principal requirements of the present investigation are adequately served by a numerical description of the test colors as they would appear to a standardized normal observer under the observational and reference conditions as defined for colorimetric purposes by the International Commission on Illumination.[3] It will be of interest, however, in the following discussion, to indicate qualitatively some changes in color perception accompanying the transition from standard conditions of observation to service conditions. In particular, an additional specification for purples will be provided to accommodate the aberration effect. Knowing the absolute intensity and color temperature of the source, and the spectral transmission

[3] Proc. 8th Session, International Commission on Illumination, Cambridge, p. 19–29 (September 1931). T. Smith and J. Guild, *The CIE colorimetric standards and their use*, Trans. Opt. Soc. **33**, 73 (1931–32). D. B. Judd, *The 1931 ICI standard observer and coordinate system for colorimetry*, J. Opt. Soc. Am. **23**, 359 (1933).

of the filters used, we may proceed then for the standard conditions by purely analytical and graphical methods to separate evaluations of the luminous and chromatic aspects of the signal colors, with reference to the ICI standard observer and specified coordinate systems.[4]

The absolute intensity of the diffusion-screen source (without filter) and its color temperature were determined by direct comparison with laboratory standards. The spectral transmission of each filter used in this investigation was measured with the Koenig-Martens spectrophotometer,[5] and luminous transmissions[6] were computed for the standard observer and source at 2,840° K. The values are recorded in column 3 of table 1, following the NBS laboratory number and manufacturer's designation of the filter in columns 1 and 2, respectively. These NBS filter numbers are also used throughout this paper to denote the corresponding signal color. Signal intensity is the product of source intensity by the luminous transmission of the filter used, and serves in the present investigation as the quantitative expression for the luminosity of the signal color, as distinct from the color quality, or chromaticity.

The chromaticity[7] of each signal color is herein evaluated with reference to two different trilinear coordinate systems. The (x, y, z) coordinates in columns 4, 5, and 6 of table 1, refer to the standard ICI system of colorimetry. The (r, g, b) coordinates in columns 7, 8, and 9 refer to the UCS (uniform chromaticity scale) system more recently devised by Judd.[8] Values on the UCS system are graphically represented for all the test colors on the equilateral triangle of figure 2. Inasmuch as the three coordinates sum to unity, by definition, only two of them need be labeled in the figure. This is done for r and g and the unused parts of the triangle are eliminated. For comparison and reference on the same diagram the locus of the pure spectrum colors is also shown, with the limiting purple line connecting the extreme spectral red and blue (violet). All real colors lie within this enclosure. Highly saturated colors are near the boundary and from thence the colors decrease progressively in saturation in the general direction of white.

The characteristic property of the UCS diagram, which is of particular utility in the present connection, is that any series of colors equally separated in chromaticity will be represented on this diagram as approximately equidistant from one another. Hence, if concentric circles be drawn in any region of the diagram all colors on the circumference of any one circle differ in chromaticity from the central color by approximately the same amount.

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[4] For the theory of the transformation from one coordinate system to another, see D. B. Judd, *Reduction of data on mixture of color stimuli*, BS J. Research **4**, 515 (1930) RP163; J. Guild, *On the fixed points of a colorimetric system*, Trans. Opt. Soc. **32**, 25 (1930–31).

[5] H. J. McNicholas, *Equipment for routine spectral transmission and reflection measurements*, BSJ. Research **1**, 793 (1928). RP 30.

[6] Luminous transmission is the ratio of the candlepower of the source-filter combination to the candlepower of the source alone, as would be measured by the standard observer with the source in operation at a color temperature of 2,840° K.

[7] The term *chromaticity* characterizes the quality of the color, as distinct from its purely luminous aspect, and is perhaps most readily visualized in terms of hue and saturation. See Report of Committee on Colorimetry for 1920–21, J. Opt. Soc. Am. & Rev. Sci. Instr. **6**, 527 (1922). *Hue* is that attribute of chromaticity which classifies all colors in their departure from gray (or white) as reddish, yellowish, greenish, etc. *Saturation* is that attribute of all colors possessing a hue, which determines their degree of departure from gray (or white). Gray (or white) is hueless and completely unsaturated; homogeneous spectrum colors possess the maximum saturation possible for a given hue. It will be convenient to refer qualitatively to the hue and saturation of the signal colors, in relation to their quantitative expression and graphical representation in trilinear coordinates.

[8] D. B. Judd, *A Maxwell triangle yielding uniform chromaticity scales*, J. Research NBS **14**, 41 (1935) RP756 or J. Opt. Soc. Am. **25**, 24 (1935).

An outstanding feature of the diagram is the proximity of the whites to the spectrum locus. Under the observational conditions of the present investigation color 8472 is found roughly to define the center of the best range of signal white. Drawing a circle with this center and tangent to the spectrum locus shows that wave lengths in the neighborhood of λ 572 are nearest in chromaticity to the signal white, and hence the least saturated of all spectrum colors. The same wave length is found by Guild [9] as that most easily confused with subjective white, for small sources and five observers. Again, it has been shown by others [10] for standard field sizes that wave lengths in

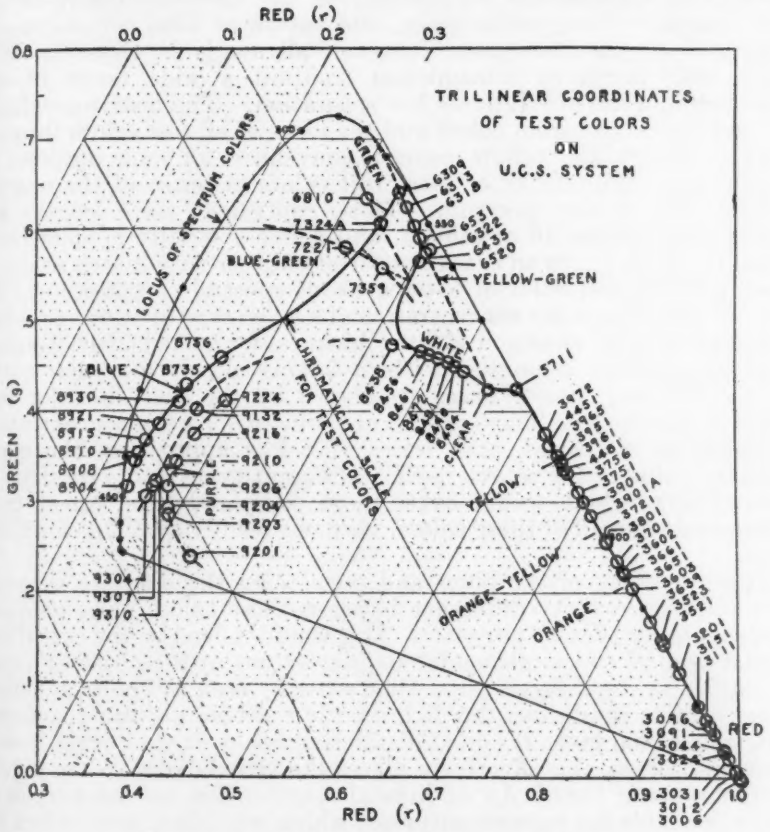

FIGURE 2.—*Trilinear coordinates of test colors.*

the range between 570 and 572 represent the spectral region of lowest saturation. In the choice of two or three signal colors between green and red the hueless and completely achromatic nature of white gives it a unique advantage over the nearby weak yellows. The identification of this signal is based solely on the observer's subjective concep-

[9] J. Guild, *On the selection of a suitable yellow glass for railway signals*, Proc. Int. Cong. Illum., Saranac Inn, New York, p. 862-876 (September 1928).

[10] I. G. Priest and F. G. Brickwedde, *The minimum perceptible colorimetric purity as a function of dominant wave length with sunlight as neutral standard*, J. Opt. Soc. Am. & Rev. Sci Instr. **13**, 306 (1926). D. McL. Purdy, *On the saturations and chromatic thresholds of the spectral colors*, Brit. J. Psychol. (Gen. Sec.) **21** (part 3), 283 (1931). L. C. Martin, F. L. Warburton, and W. J. Morgan, *Determination of the sensitiveness of the eye to differences in the saturation of colours*, Medical Research Council, Reports of the Committee upon the Physiology of Vision, XIII, Special Report Series, no. 188, London (1933).

tion of whiteness. It is apparent that little or no advantage would be gained by use of a weak yellow in place of white in a six-color signal system.

It is well known that sensibility to hue differences is greater for colors of high saturation. Hence, for maximum distinctiveness from one another and from white, the chromatic colors should lie as close as possible to the spectrum locus and, in so far as the given UCS diagram applies to colors of "point" sources, the best choice of colors would be that which separates them equally on this diagram.

By use of only commercially available colored-glass filters it is possible to approximate very closely to the spectrum colors in the red, orange, yellow, yellow-green, and saturated blue regions of the diagram. In the blue-green, however, all available glass filters of appreciable luminous transmission transmit a wide range of the spectrum and are of relatively low saturation. The near coincidence of the locus of spectrum colors and the locus of all test colors through the red, orange, and yellow makes it convenient for some purposes to express the chromaticity of these test colors in terms of the nearest wave length in the spectrum. These equivalent wave lengths are recorded in column 10 of table 1, and define a strictly homogeneous stimulus which yields an exact or nearest chromaticity match with the corresponding test color of heterogeneous spectral composition. By regular variation in the concentration of a given type of coloring matter in the glass, or by variation of filter thickness for a fixed concentration, a series of colors is produced which follows closely a regular curve in the diagram. Such curves are shown by the dash lines for two types of purples, the blues, greens, and whites. As the concentration or thickness decreases, each series of colors approaches the chromaticity value of the source itself. Different types and variations of green filters, which would cover more adequately the broad two-dimensional spread of these colors, were not readily available for these tests.

The proximity of the blues and purples on the diagram suggests that the chromaticity difference between these colors must be quite inadequate for present purposes. This would indeed be the case if the source were of appreciable solid angular extent at the observer's eye, as implied in the diagram; but when actually seen as "point" sources under service conditions the dichromatic red-blue pattern characterizing this signal gives it added distinctiveness over the purely monochromatic blues, and effectively places the signal closer to the purely monochromatic reds. An additional specification for the purples is hence desirable for present purposes, which will place these colors on a linear scale extending between the extreme blue and red. The required parameter is satisfactorily provided by the ratio of the red-light transmission (T_r) to the entire luminous transmission (T_w). The values of this ratio are given in the lower part of column 10, table 1, and the relation to T_w shown in figure 3, for the two types of purple-glass filters employed in this investigation.

TABLE 1.—*Description of test colors*

NBS number of filters	Maker's designation of filters	Colorimetric properties of source-filter combinations referred to the 1931 ICI standard observer and source at 2,840° K							
		Luminous transmission T_v	Trilinear coordinates						Wave length for reds and yellows λ
			ICI system (standard)			UCS system (Judd)			
			x	y	z	r	g	b	
1	2	3	4	5	6	7	8	9	10
3006	Jena *RG8*	0.0006	0.7363	0.2637	0.0000	1.0000	0.0000	0.0000	700
3012	Corn. 241, 17.5%	.0095	.7326	.2674	.0000	.9933	.0067	.0000	690
3031	Corn. 241, 46%	.025	.7281	.2718	.0000	.9795	.0205	.0000	655
3024	Corn. 241, 34.5%	.020	.7258	.2742	.0000	.9722	.0278	.0000	650
3044	Corn. 241, 68%	.036	.7252	.2748	.0000	.9704	.0296	.0000	649
3091	Corn. 243, 126%	.074	.7193	.2807	.0000	.9529	.0471	.0000	641
3096	Kopp R. R. Red	.069	.7164	.2836	.0000	.9444	.0556	.0000	637
3111	Corn. 243, 165%	.095	.7143	.2857	.0000	.9384	.0616	.0000	635
3151	Corn. 243, 218%	.127	.7088	.2913	.0001	.9228	.0772	.0000	631
3201	Corn. 246, 78%	.177	.6953	.3046	.0001	.8871	.1128	.0000	622
3521	Corn. 246, 104%	.226	.6829	.3169	.0002	.8564	.1435	.0001	616
3523	Corn. 246, 100%	.217	.6812	.3186	.0002	.8523	.1476	.0001	615
3639	Corn. 246, 123%	.266	.6720	.3278	.0002	.8309	.1691	.0001	612
3603	Corn. 246, 142%	.326	.6561	.3436	.0003	.7961	.2039	.0001	607
3651	Corn. 348, 155%	.340	.6485	.3512	.0003	.7803	.2196	.0001	605
3661	Corn. 348	.338	.6476	.3521	.0003	.7785	.2214	.0001	605
3602	Corn. 246	.341	.6471	.3526	.0003	.7775	.2224	.0001	605
3701		.364	.6411	.3585	.0004	.7656	.2343	.0001	603
3801	Jena *OG2*	.452	.6304	.3693	.0004	.7449	.2550	.0001	601
3721	Corn. 350, *Y6.3*	.427	.6297	.3699	.0004	.7437	.2562	.0001	601
3901A	NBS (3901+3756)	.354	.6137	.3858	.0006	.7149	.2849	.0001	597
3901	Corn. *Y5*	.463	.6059	.3935	.0007	.6997	.3002	.0002	596
3751	Corn. 349, *Y5*	.540	.5984	.4009	.0007	.6893	.3105	.0002	595
3756	Corn. 350, *Y3.5*	.555	.5852	.4138	.0010	.6685	.3312	.0002	592
4481	Corn. 330	.370	.5801	.4151	.0048	.6627	.3361	.0011	591
3961	Corn. 350, *Y3.0*	.612	.5776	.4212	.0012	.6571	.3426	.0002	590
3951	Corn. *Y3.0*	.592	.5755	.4233	.0012	.6540	.3457	.0003	590
3965	Corn. 350, *Y2.8*	.651	.5724	.4262	.0014	.6494	.3503	.0003	589
4451	Corn. 330	.488	.5583	.4295	.0122	.6347	.3625	.0028	587
3972	Corn. 351, *Y2.1*	.725	.5541	.4436	.0023	.6240	.3755	.0005	586
5711	Jena *G.G.11*	.873	.5065	.4723	.0212	.5710	.4246	.0044	580
Clear	(Colorless glass) Source 2,840° K	.920	.4476	.4075	.1449	.5434	.4239	.0327	
8494	Corn. 557, 284%	.567	.4030	.3907	.2063	.5086	.4441	.0474	
8490	Corn. 557, 247%	.490	.3881	.3829	.2290	.4973	.4496	.0531	
8481	Corn. 557, 216%	.429	.3750	.3750	.2500	.4874	.4540	.0586	
8472	Corn. 557, 190%	.376	.3601	.3649	.2750	.4762	.4584	.0653	
8461	Corn. 557, 160%	.320	.3446	.3527	.3027	.4647	.4621	.0732	
8456	Corn. 557, 148%	.294	.3330	.3472	.3198	.4549	.4672	.0779	
8438	Corn. 557, 99%	.199	.2921	.3078	.4001	.4227	.4734	.1039	
7359	Corn. 440, 206%	.269	.2458	.4152	.3390	.3706	.5578	.0716	
6520	Kopp *GX*	.098	.3018	.5288	.1693	.4039	.5655	.0306	
6435	Corn. 401	.200	.3098	.5734	.1168	.4054	.5747	.0199	
6322	Corn. 401, 93%	.117	.3182	.6020	.0798	.4085	.5779	.0136	
6531	Jena *VG2*	.161	.2906	.5996	.1098	.3911	.5909	.0180	
6318	Corn. 401, 71%	.093	.2742	.6259	.0999	.3795	.6046	.0158	
6313	Corn. 401	.067	.2446	.6643	.0908	.3609	.6255	.0137	
6309	Corn. 401, 37%	.049	.2202	.6929	.0869	.3468	.6406	.0126	
6810	Kopp *G.B*	.045	.1721	.5442	.2837	.3171	.6340	.0489	
7324A	Corn. 440+NBS 4306	.082	.2136	.5184	.2680	.3442	.6076	.0482	
7221	Corn. 440, 80%	.109	.1855	.3755	.4390	.3220	.5805	.0975	
8756	Corn. 556, 126%	.034	.1510	.1202	.7288	.2595	.4591	.2814	
8735	Corn. 556, 79%	.021	.1439	.0846	.7715	.2391	.4293	.3316	$\frac{T_r}{T_v}$ for
8930	Corn. 554	.016	.1473	.0728	.7799	.2406	.4100	.3494	purples
8921	Corn. 554, 36%	.011	.1464	.0550	.7986	.2327	.3865	.3808	
8915	Corn. 554, 24.8%	.0075	.1465	.0432	.8104	.2281	.3682	.4037	
8910	Corn. 554, 18.4%	.0056	.1483	.0360	.8157	.2282	.3534	.4184	
8908	Corn. 554, 14.4%	.0047	.1497	.0325	.8178	.2294	.3450	.4256	
8904	Corn. 511, 9.2%	.0028	.1550	.0224	.8226	.2351	.3172	.4476	0.000
9132	Corn. 555, 127%	.020	.1596	.0796	.7606	.2626	.4022	.3352	.071
9224	Kopp no. 2, 1.35 mm	.011	.1718	.1004	.7278	.2861	.4125	.3014	.110
9307	Corn. 555, 27.7%	.0039	.1661	.0325	.8014	.2606	.3180	.4214	.123
9216	Kopp no. 2, 1.60 mm	.0080	.1683	.0683	.7633	.2741	.3745	.3514	.132
9310	Corn. 585, 37%	.0049	.1657	.0348	.7995	.2605	.3230	.4165	.132
9304	Corn. 555, 20.6%	.0030	.1666	.0270	.8064	.2598	.3064	.4338	.158
9210	Kopp no. 2, 1.93 mm	.0053	.1686	.0494	.7820	.2701	.3443	.3856	.159
9206	Kopp no. 2, 2.33 mm	.0032	.1731	.0381	.7887	.2755	.3171	.4074	.235
9204	Kopp no. 2, 2.89 mm	.0019	.1807	.0322	.7871	.2887	.2929	.4183	.340
9203	Kopp no. 2, 3.12 mm	.0015	.1830	.0306	.7863	.2931	.2857	.4212	.368
9201	Kopp no. 2, 5.83 mm	.0004	.2055	.0275	.7670	.3381	.2395	.4224	.664
3006	(See previous entry)								1.000

In further reference to the change in the appearance and chromaticity of the signal lights, when compared under actual service conditions and under standard laboratory conditions, it was noted qualitatively (by memory comparison) during the course of this investigation that on the range the orange and orange-yellow signals appeared less saturated and slightly shifted in hue toward the yellow. Similarly, it was observed that the greens under service conditions decreased considerably in saturation and the normal hue difference between the greens and blues was considerably reduced. In this connection it may be noted also that the progressive spreading of the signals through the green and blue results in a corresponding progressive decrease in retinal illumination for these signals. Since this decrease would be greater for the shorter wave lengths it is possible that this aberration effect may result in a slight hue shift of the less saturated blues toward the green.

The combined effects of decreasing field size and retinal illumination on the saturation of the pure spectrum colors was investigated experi-

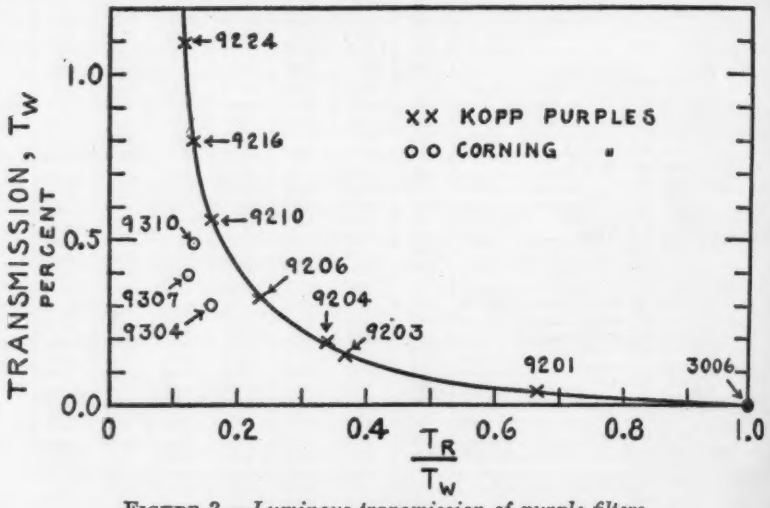

FIGURE 3.—*Luminous transmission of purple filters.*

mentally by Purdy.[11] For such changes in observational conditions it was found that the color differences between the various parts of the spectrum were greatly reduced until the threshold of chromatic visibility was reached, below which all parts of the spectrum except the long-wave end appeared achromatic or gray. The long wave end changed with decreasing retinal illumination from strong to weak red, but at the threshold of chromatic visibility passed directly from weak red to complete invisibility. This region has the lowest chromatic threshold with respect to retinal illumination and is followed in increasing order of the threshold by parts which normally appear orange, yellow, and blue. Green exhibits the highest chromatic threshold, and in the present investigation green signals appeared greatly desaturated at low intensities on the test range. Some of the field observations to be described were made for retinal illuminations

[11] D. McL. Purdy, *On the saturation and chromatic thresholds of the spectral colours*, Brit. J. Psychol. (Gen. Sec.) **21**, 283 (1931).

below and not far above the chromatic thresholds for the red, green, blue, and purple signals.

These considerations afford a qualitative explanation of the difficulties experienced in the discrimination between greens and blues in the present investigation, notwithstanding the wide separation of these colors on the diagram in figure 2; for, under service conditions, the actual chromaticity difference between these colors is considerably less than is indicated on the diagram. The situation may be expressed by saying that the locus of the spectrum colors on a uniform-chromaticity-scale diagram, established for actual service conditions, would show, relative to the given UCS diagram of figure 2, a slightly greater separation between the test colors throughout the orange and orange-yellow and a considerably decreased separation between the strong greens and blues. Accompanying this change there would be undoubtedly a general reduction in the total area included by the spectrum locus and the purple line. It will be evident from the observations to be described that it is impossible to interpose a distinctive "point" signal between the strong blue and the yellow-green signals. Another practical difficulty in this connection is involved in the im-

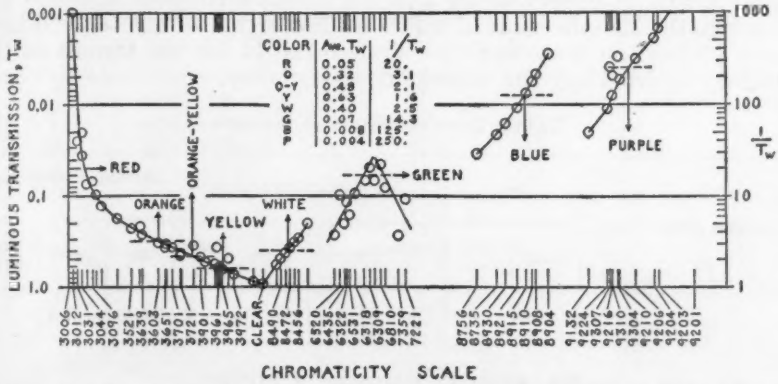

FIGURE 4.—*Luminous transmission of filters used in the production of light signals.*

possibility of producing highly saturated blue-greens by use of commercial colored-glass filters of sufficient luminous transmission.

The heavy solid line on the (r, g) diagram, passing through the entire ranges of the reds, yellows, whites, greens, and blues, is drawn to provide a linear chromaticity scale along which all the test colors may be arranged in a logical regular order, and the results of the field observations and other information readily presented in graphical form. The scale is laid out along the horizontal axes in figures 4 and 6, with the spacing of all colors (except the purples) always proportional in each figure to their spacing (or projected spacing) along the curve in figure 2. At the extreme end of the blues (color 8904) the chromaticity scale is extended through the purples to the extreme red (color 3006), with the spacing of colors now proportional to the square root of the T_r/T_w ratio for these colors. This particular spacing for the purples is arbitrarily chosen wholly for convenience in the graphical representations.

Figure 4 shows the variation in luminous transmission of all filters used in the production of colors along the linear chromaticity scale.

Transmissions are represented on a logarithmic scale. The right-hand ordinate scale indicates the relative source intensity required behind each filter for the production of constant signal intensities. Thus, if a 1-candlepower lamp suffices for the filter producing the white signal, about 50 and 100 candles are required, respectively, for the average blue and purple filters.

A total of 38 observers participated in the recording of the field observations. Their distribution with respect to sex, age, and other characteristics is shown in table 2. Not all observers were available for the color-blindness tests, but the field observations do not show any obvious or consistent abnormality between any of the observers in the classification of the test colors. All the observers may be regarded as of normal color vision in the ordinary sense of the word. Several observers had some previous experience in the matching of colors or discrimination between them, but the majority had no experience or special training in this respect. In the same test an observer with no experience whatever was sometimes more consistent and precise in the color classification than another with considerable experience. There is no evidence that experience is an important characteristic of observers for this work. The effect of age was apparent in the classification of colors for low signal intensities. Those above 40 in these tests were the first to fail to see the signals as the intensity approached the threshold of visibility.

TABLE 2.—*Description of observers*

Number of observers	Sex		Age distribution (years)				Ishihara color-blindness test		
	Male	Female	Below 20	20 to 30	30 to 40	Above 40	Passed	Failed	Not tested
38	29	9	3	19	13	3	21	0	17

IV. FIELD OBSERVATIONS

In the assignment of a series of test colors to given color classes by a group of normal observers, chromaticity, or hue in particular, is in most cases the primary discrimination factor determining the classification. In the case of purples the dichromatic hue pattern becomes the dominant criterion for recognition. The differential spreading of the purple and the monochromatic signal lights is a minor influence in this respect. The subjective criterion of chromaticity is modified by the following secondary factors and test conditions, which are listed below in their estimated order of importance.

(1) The association, through color education and memory, of a given test color with all adjacent colors included in the test. The effect is a maximum when the test colors cover the entire chromaticity range between adjacent color classes; it is reduced to a minimum when the test colors define only the maximum permissible tolerances in the chromaticity ranges of the given color classes.

(2) The variation in individual color-vision characteristics and association tendencies within a group of normal observers.

(3) The range of signal intensities, or equivalent distances, over which the signal colors must be positively identified.

(4) The weather conditions affecting atmospheric transmission or luminous contrasts in the field of view.

A systematic survey of the separate effects of each factor on the color classifications was impractical under the circumstances of the present investigation. Simultaneous uncontrolled variations in conditions occurred in such manner as often to prevent the true effect being derived from the observations. Such information as may be gleaned from the whole body of data will appear throughout the discussion.

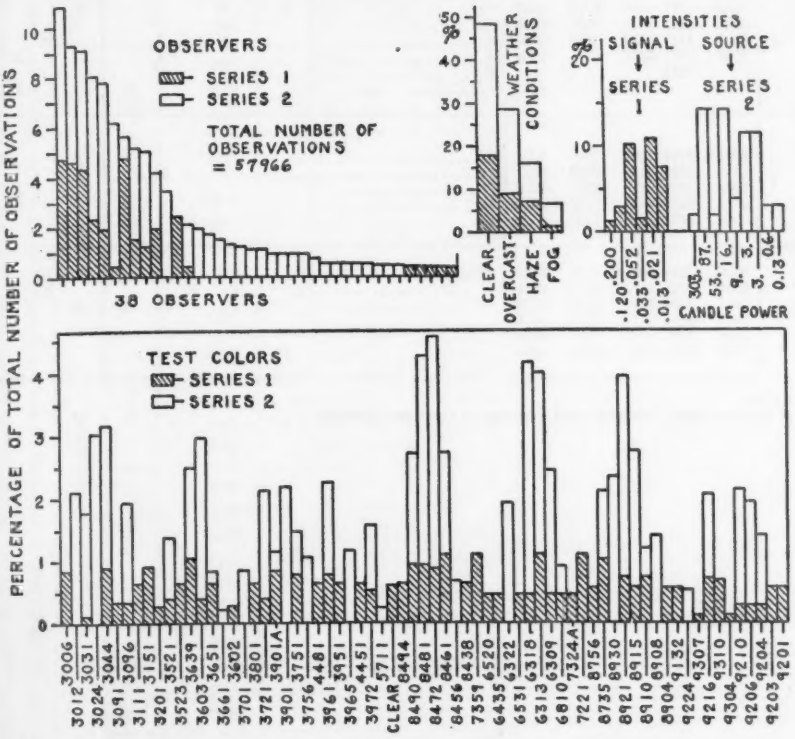

FIGURE 5.—*Distribution of field observations over the range of test colors, observers, weather conditions, and signal intensities covered in the present investigation.*

In the selection of the two six-color sets with tolerance limits nearly 58,000 single color classifications were made by the 38 different observers. These observations are included in two series of test runs and are distributed among the different test colors, observers, signal or source intensities, and weather conditions, as depicted in the diagram of figure 5. Inasmuch as only a limited number of observations and range of test conditions could be included in one run with a given group of observers, both series of observations consisted of several runs which were made under varying conditions, as indicated in tables 3, 4, 5, and 6.

TABLE 3.—*Arrangement of field observations in series 1, for different color sets, signal intensities, and weather conditions*

Test no.	Colors tested	Run no.	Signal intensity (candles)						Weather			
			0.200	.120	.052	.033	.021	.013	Clear	Overcast	Haze	Fog
1	3006 3639 (•) 7221 9132 3044 3651 8461 8756 9216 3111 3801 8438 8735 9310 3151 4481 7359 8904 9203 3523 4451 6313 9201 3951	1 2 3 4 5 6 7										
2	3901A 8494 7359 6313 8735 3751 8490 6520 6309 8921 3961 8481 6435 6810 8915 3972 8472 6531 7324A 8910 (•) 8461 6318 7221	13 14 16 18										
3	3006 3201 3901A 8481 9216 3031 3521 3751 8472 9310 3044 3639 3961 8921 9304 3091 3603 3972 8915 9210 3096 3602 8494 8910 9206 3151 3721 8490 9307 9204	15 17 19										

• Clear.
× denotes signal intensity and weather for the run indicated.

TABLE 4.—*Arrangement of field observations in series 2, for set P colors, different source intensities, and weather conditions*

[× denotes colors, intensities, and weather for the run indicated. 0 denotes higher intensities used for blues and purples only]

Run number	Colors tested								Source intensity (candles)									Weather				
	Red		Yellow		White		Green	Blue	Purple													
	3012	3031	3024	3044	3096	3603	3721	3756	3961	8490	8481	8472	8461	8456	6322	6318	6313	6309	6810	8736	8930	8921	8916	8910	8908	9224	9216	9210	9206	9204	303.	87.	63.	16.	9.	3.	.6	.13	Clear	Overcast	Haze	Fog
24	×																		×																						
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TABLE 5.—*Arrangement of field observations in series 2, for set O colors, different source intensities, and weather conditions*

[X denotes the colors, intensities, and weather for the run indicated. O denotes higher intensities used for blues only]

Run number	Colors tested										Source intensity (candles)										Weather				
	Red		Orange		Yellow		White		Green		Blue														
	3012	3024	3031	3044	3621	3639	3603	3661	3701	3751	3901	3961	3965	3972	6711	8490	8481	8472	8461	8456	6322	6318	6313	6309	6810	8735	8830	8921	8915	8910	8908	303	57	13	16	9	3	.6	.13	Clear.	Overcast.	Haze.	Fog.
21				XXX																				XXX						XXX	XX							XXX			
22												XX						XXXX						XX	XX			XXX									XX			
23		X	X																								X													
25																																								
26												X			X																									
29		XXXX	XXXX			XXXX	XXX		XXX			X																											
32		XXXX	XXXX			XX	XXX		XX	X		X																											
35						X																																	
38		XX	XXXX			X	XXX		XX					XX					XX																				
39		XXXX	XXXX			X	XXX		XX	X				XX					XX																				
40						X								X																									
47				X		X				X				X						X																			

TABLE 6.—*Signal intensities*

	SERIES 2								SERIES 1
Color	*R*	*O*	*O-Y*	*Y*	*W*	*G*	*B*	*P*	Signal intensity (candles) for all colors
Avg. ^aT_w	0.05	0.32	0.48	0.63	0.40	0.07	0.008	0.004	
Source intensity (candles)	Signal intensity (candles) = source intensity × avg T_w. Approximately 79 percent of all observations of series 2 were made at source intensities of 87, 16, and 3 candles								
303 [b]							2.4	1.2	
87	4	28	42	55	35	6	.7	.3	
53 [b]							.4	.2	
16	.8	5	8	10	6	1	.1	.06	0.20
9 [b]							.07	.04	.12
3	.2	1.0	1.5	1.9	1.2	.2	.02	.01	.052
3 [c]									.033
.6 [c]	.03	.2	.3	.4	.2	.04	.005	.002	.021
.13 [c]	.006	.04	.06	.08	.05	.009	.001	.001	.013

[a] Average luminous transmission of filters. See figure 4.
[b] Source intensities used only for blue and purple of set *P*.
[c] Source intensities used only in 1 run for each 6-color set.

The test colors of series 1 were selected to cover in small steps the entire range of chromaticities along the scale in figure 6. The fulfilment of this condition depended, of course, on the availability of suitable colored-glass filters. The chief difficulty in this respect occurred throughout the blue-green region. However, such breaks as occur in the sequence of colors are in regions found to be unsuitable for the signal colors. In the classification of this series of colors the effect of color association is large, but it was desired to determine under this adverse condition the regions of maximum signal efficiency for all members of the two six-color sets. In the observations of series 2 these selected regions were reduced considerably and the limits adjusted to define the maximum acceptable tolerance ranges for members of each six-color set.

1. CLASSIFICATION OF TEST COLORS, SERIES 1

In test 1, series 1 (table 3), the range of the purples, oranges, and yellows was covered in small steps, but only three representative colors were included in each of the red, white, green, and blue color classes. Observers were thus free to assign each test color to any one of the seven permitted classes. It was desired to indicate in this test the best value of T_r/T_w for the purples and to select those colors which the observers as a group most consistently chose to identify as orange and yellow in distinction from red and white. In test 2 the colors were chosen with the specific purpose of determining the best green and the extent of this color region most suitable for use on equal terms with yellow, white, and blue. In test 3 the colors were spaced to cover more uniformly all classes except the green, which was omitted only to reduce the total number of colors in the test. Some variation in observers and weather occurred in these tests, but in each run all signals appeared at the same intensity level, so that all signals had the same intensity advantage in the classification. The effect of the number of permitted color classes was apparent in these tests. Because of the absence of green in test 3 and the elimination of this

possible classification it was found that the errors in the classification of the whites were thrown more to the blue in this test than they were in tests 1 or 2. The reverse effect was shown in the classification of the blues. Similarly, in test 2, the absence of red and orange caused the classification of the end yellows to be more perfect than they would have been had the orange and red classifications been permitted. In general, the colors called orange and yellow were less saturated in test 1 than in test 3.

Taking these variations and all test conditions into consideration, a weighted average of all observations in series 1 was made, and adjusted so that the numbers representing different classifications of each color summed to 100 and defined the smooth continuous curves shown in the lower part of figure 6.

The following remarks are based on the results of this series of tests:

(1) Purples in the range between 9206 and 9204 contain the best proportion between red and blue. On the whole these purples are quite positively identified by all observers under the most adverse conditions of observation, provided the signal intensity is comparable with that of the other colors, as it was in this series of tests. Purples are, naturally, most often confused with red and blue. This is particularly the case for observers who do not completely resolve the blue and red components of purple and hence must discriminate between blue, purple, and red without full benefit of the aberration effect. Bluish purples are also slightly confused with white and green by a few observers.

(2) It is seen, conversely, that a strong blue (8904) or a strong red (3006) may be erroneously classified as purple, even though the blue signal contains no long-wave light and the red signal contains no short-wave light. Hence, a signal system including red, blue, and purple must limit the hue of the red and blue on the purple side and avoid low limits of signal intensity.

(3) A highly saturated "sextant" green (6318 to 6309) is required for maximum possible distinctiveness from a saturated blue or from white. The discrimination between white, green, and blue becomes unsatisfactory in passing from the sextant green to the blue-greens (7359 and 7221) of the type commonly employed in street and railroad signals. It is apparent that the saturated colors in the neighborhood of 6810, 6318, and 6309 must be employed in a signal system wherein blue enters on equal terms with green and white. The discrimination between green and white is good until the saturation of the green decreases to that of color 6435, approximately.

(4) The orange and yellow are definitely the least distinctive colors of this seven-color set, showing the maximum confusion between one another and with the adjacent red and white. It is noted that the points of maximum confusion between orange and yellow and between red and white are both in the neighborhood of 600 $m\mu$ on the wavelength scale, which is also the wave length found by Guild [12] to represent the (homogeneous) spectrum color most efficiently discriminated from spectrum red and the "white" of a paraffin lamp. The dash-line curve in the figure is the sum of the ordinates for the orange and yellow and is drawn on the assumption that it would represent the field observations if only one color class had been permitted between

[12] J. Guild, *On the selection of a suitable yellow glass for railway signals*, Proc. Int. Cong. Illum., Saranac Inn, N. Y., p. 862-887 (September 1928).

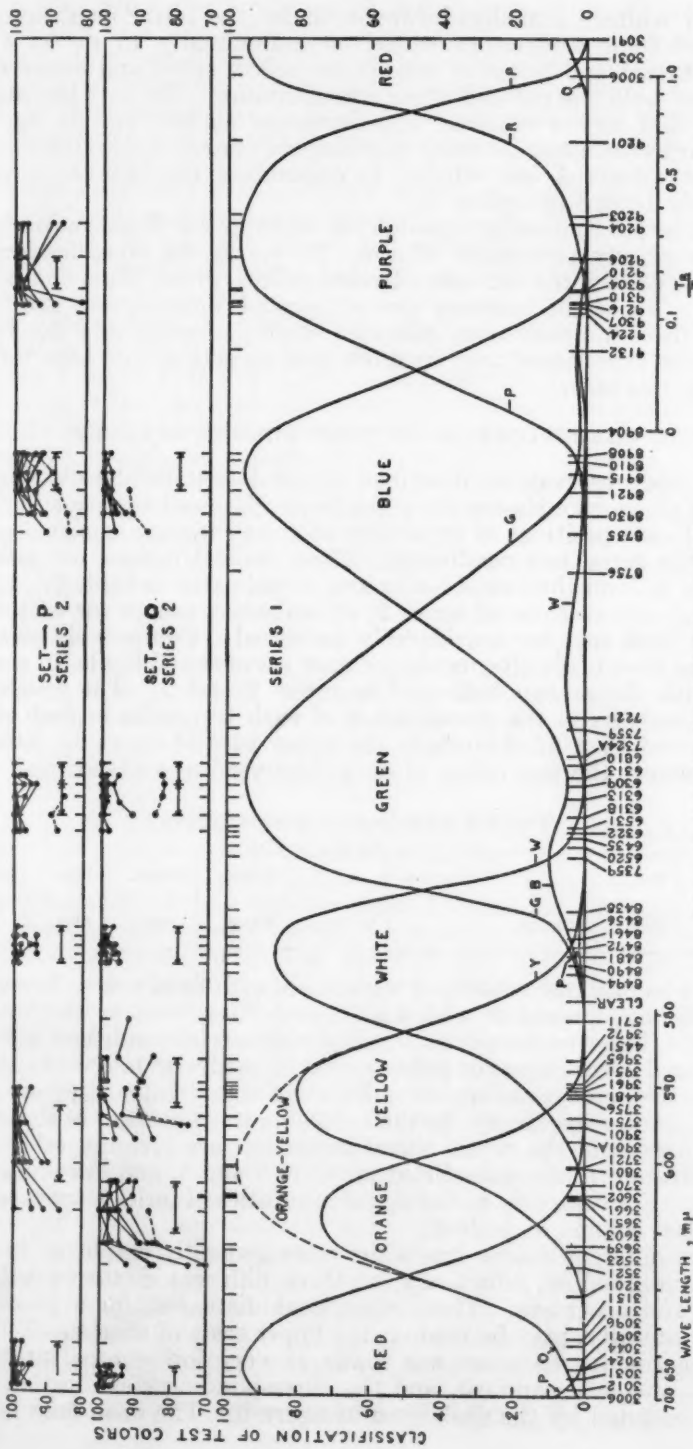

FIGURE 6.—*Color classification of light signals.*

red and white. Actually, however, under the latter condition, the effect of color association would be undoubtedly to decrease the lateral extent and height of the orange-yellow curve and increase the spread of both the red and white classifications. We may tentatively choose that region centered approximately at 600 mμ as the best color for use in a low-intensity point-signal system employing but one color between red and white. It determines the orange-yellow of set *P*, as defined in section I.

(5) The discriminating criterion for white in the classification is the absence of any perception of hue. Errors in the classification are therefore distributed between adjacent yellow, green, blue, and purple classes. The slight tendency toward purple is unimportant and arises chiefly from the aberration effect for white, as previously described, which was experienced only by a few new observers, who soon learned to avoid this error.

2. CLASSIFICATION OF TEST COLORS, SERIES 2

The field observations described above determine the distribution of eight given color classes along the linear chromaticity scale in figure 6, and locate positions of maximum efficiency for use as signal colors under the given test conditions. These central regions are now regrouped to form the two six-color sets as indicated in table 7. In the following observations of series 2, chromaticity ranges for each color class in both sets are considerably narrowed. Comparable observations are then made alternately for each set of signal lights, in accordance with the scheme indicated in tables 4 and 5. The number of correct answers in the classification of each test color in each run is represented by a filled circle in the upper part of figure 6. Straight lines connect the test colors of each class used in a given run.

TABLE 7.—*Designation of signal colors*

Set *P*.....	Red.....	.....	Orange-yellow.	.....	White.....	Green.....	Blue.....	Purple.
Set *O*.....	Red.....	Orange.....	.....	Yellow.....	White.....	Green.....	Blue.....	.....

The observations of series 2 were made with fixed source intensities for each run, instead of with fixed signal intensities, as employed in series 1. This was done in conformity with service conditions in which the colored cover glasses or globes would be used with lamps of approximately the same candlepower. Relative signal intensities are then proportional, respectively, to the luminous transmissions of the cover-glass filters; and the actual signal intensities are given in table 6 for the fixed source intensities listed in tables 4 and 5, and in column 1 of table 6. For comparison, the signal intensities of series 1 are repeated in the last column of table 6.

Three different source intensities were generally employed in each run, corresponding, effectively, to three different distances between source and observers. These equivalent distances, for a fixed 6-cp source intensity, may be read on the upper scale of abscissas in figure 9. One run for each set was made at very low source intensities (3, 0.6, and 0.13 candles), and the corresponding classification data are represented by the dash lines in figure 6. The dash lines for the

purple fell below the boundary of the diagram. Signal intensities were in this case well below the chromatic threshold of visibility for the majority of observers at 950 feet from the source. This was also the case to a lesser degree for some observers in the blue, green, and red. All data represented in figure 6 exclude such cases in which no color classification of the signals was possible because of low intensity.

It is seen that the reduction in the chromaticity range of the test colors for each class has markedly increased the distinctiveness of each signal. The effect of color association is greatly reduced. Again, as in series 1, we find the orange and yellow of set *O* to be the least distinctive of the signal colors, but the orange-yellow of set *P* is quite satisfactory in this respect.

The observations of series 2 comprise 66 percent of the total and were made several months after series 1 was completed. Reference to figure 5 shows that the 11 out of 38 observers who participated in both series of tests also made 74 percent of all the observations. The range of signal intensities was greater in series 2 and very much higher throughout the orange, yellow, and white (table 6). A later analysis of the field observations (section V) will show that the signals throughout the orange and yellow tend to shift toward the red at higher intensities. This intensity shift is manifested in figure 6 by a slight countershift to the white in the position of maximum distinctiveness for the orange, orange-yellow, and yellow of series 2. Arrows in the figure (for series 2) indicate tolerance ranges adopted for the signal colors in each set. With due consideration for the intensity shift it is seen that both series of field tests are essentially in agreement with respect to the choice of the region of maximum efficiency for each signal color. A shift of the purple limits towards the blue was found to be feasible to gain the advantage of higher luminous transmission in the filters.

V. EFFECT OF SIGNAL INTENSITY ON COLOR DISCRIMINATION

The effects of varying weather conditions on the appearance and color classification of the signals is manifested chiefly through a corresponding variation in the absolute and spectral atmospheric absorption and scattering. In the present investigation no absorption or scattering measurements were made and only 7 percent of all field observations were recorded under weather conditions for which any marked selective effect would be expected on a test range of 950 feet. Under the most adverse weather conditions of the present field tests a greater spread in the classification of the signals was observed, but any change in the color classification which might be attributed to selective atmospheric absorption or scattering was small, if present at all, and could not be differentiated definitely from the more pronounced effects of the reduced signal intensity.

If a given test signal is assumed nominally to belong to a particular color classification, say orange, it is shown by the curves in the lower part of figure 6 that the classification by the group of observers is unequally distributed between the nominal and adjacent color classes. For present purposes some convenient parameter is required to indicate the shift in this color classification with changing signal intensity. Such an indication, for a given test color, is afforded by the percentage

of unbalanced errors to the left, or to the right, of the nominal classification. The left and right sense is herein referred to corresponding directions along the chromaticity scale of figure 6. Thus, a 100-percent shift to the left for color 3523, which is nominally orange, would throw this color wholly into the red classification. The effect of signal intensity on the shift in color classification is represented graphically in figures 7 and 8.

The most pronounced effect with increasing signal intensity is the general shift toward the red in the orange and yellow. The greater magnitude of the shift for the observations of series 1 (fig. 7) is consistent with the greater spread or uncertainty in the classification of these colors at a given intensity level. The spread or confusion in the classification actually increases from medium to highest signal intensities (fig. 8). It was observed by Guild,[13] for a small source at

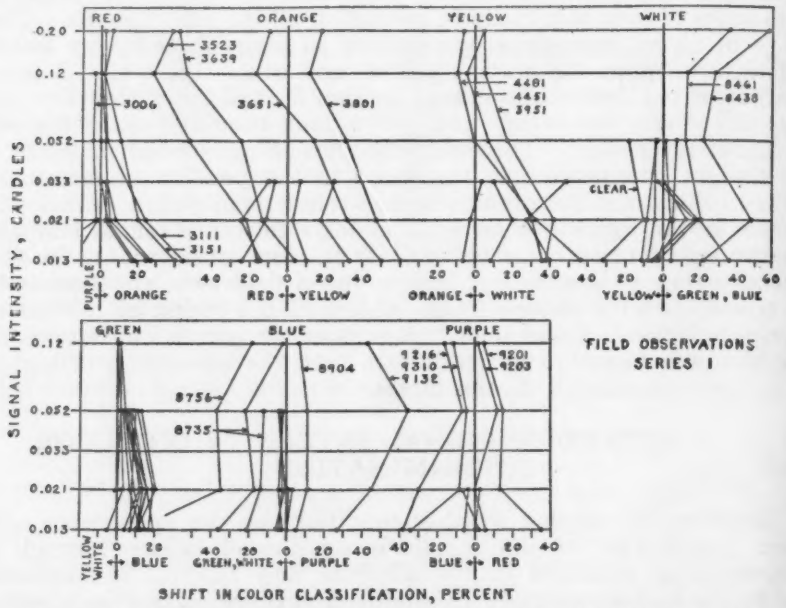

FIGURE 7.—*Effect of signal intensity on the color classification in series 1.*

1,200 feet, that the best (homogeneous) spectrum yellow for use between red and white also shifted away from red with increasing signal intensity. The present investigation is in substantial agreement with Guild in showing that whites are fairly stable over the range of intensities investigated with a slight tendency toward yellow at lowest intensities.

Another definite intensity effect is the shift of the saturated greens toward the blue for decreasing signal intensities. The less saturated green (6322) tends to shift toward the white and yellow. A reverse shift from the lighter blues toward green is indicated. Likewise, there is a shift of bluish purples toward blue and reddish purples toward red. A tendency is noted for reds to be classed as orange at the lowest and highest signal intensities.

[13] J. Guild, *On the selection of a suitable yellow glass for railway signals*, Proc. Int. Cong. Illum., Saranac Inn, N. Y., pp. 862-887 (September 1928).

In the observations of series 1 (fig. 7 and table 3) the variations in signal intensity occurred from one run to another and were accompanied by simultaneous variations in time, associated test colors, weather, and observers. In the observations of series 2, on the other hand, the intensity effect is completely disentangled from any accompanying effects of other test conditions; for a given set of signals was always presented (singly) in each run at three different source intensities to the same group of observers under the same weather and other test conditions (fig. 8, and tables 4 and 5).

VI. SELECTION OF SIGNAL COLORS AND TOLERANCES

The range of permissible chromaticity variation for white is determined in each of the two six-color sets primarily by the absence of

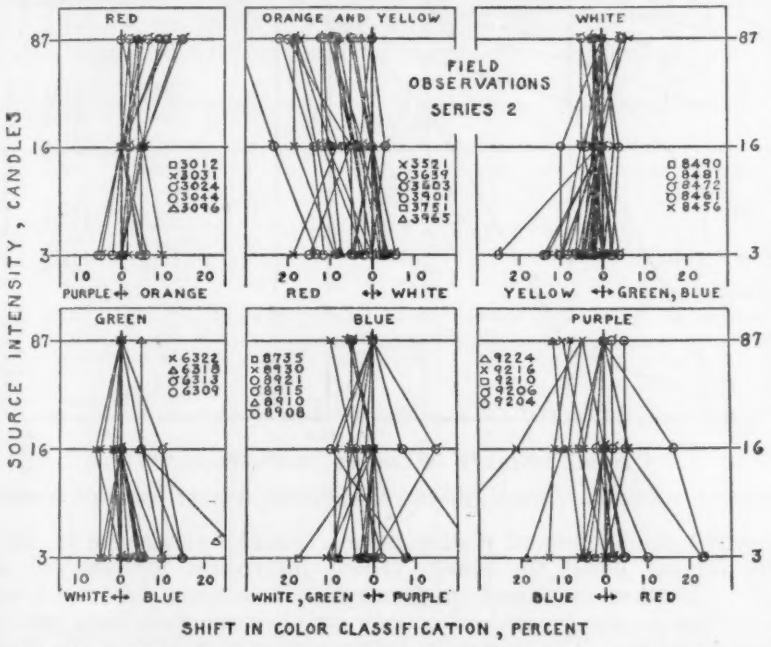

FIGURE 8.—*Effect of source intensity on the color classification in series 2.*

any readily recognized hue by the group of normal observers. Having selected suitable limits for white on this subjective basis it is obvious that the limits for green and blue may be chosen the same likewise in both signal systems. The green (or light) limit for blue is selected for minimum confusion with green, and the tolerance permissible toward the stronger blue is determined by filter transmission and the condition that no excessive confusion with purple occurs in set *P*. These two objects are accomplished with one set of limits. Purple limits are chosen to minimize confusion with blue and red and yet gain as much as possible in filter transmission. Hence, in the observations of series 2, the purple range was shifted as far as practicable toward the blue; that is, to lower values of T_r/T_w (fig. 3). Likewise, to gain the maximum advantage in filter transmission, red may be shifted farther toward the orange in set *P* than in set *O*, but the purple

(or dark) limit is again determined by confusion with purple and low filter transmission. The chromaticity tolerances to be permitted in practice must be decided also in relation to manufacturing problems for the colored glassware, and minimum ranges employed in the tests of series 2 were chosen with due consideration to such restrictions. The choice was guided in this respect by the experience of manufacturers in the supply of signal glass for American railroads.

It has been shown that the orange and yellow of set *O* are the least distinctive of all the signal colors. The discrimination between red, orange, yellow and white might be improved somewhat by further reducing the permissible tolerances in the orange and yellow; but this would markedly increase the cost of the glassware and would then

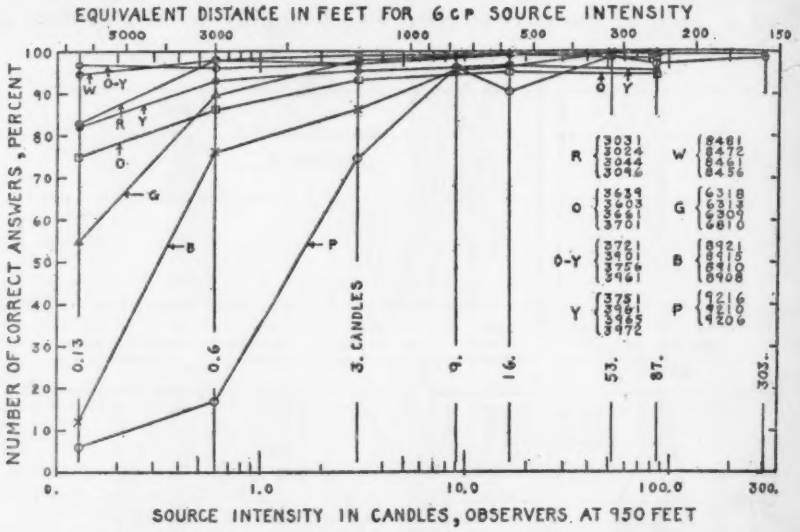

FIGURE 9.—*Relation of signal efficiency to source intensity, or equivalent distance.*

not yield the degree of distinctiveness readily attainable in set *P* with but one color, the orange-yellow, interposed between red and white. Further reduction in permissible tolerances for the orange and yellow is also limited effectively by observer variations and the intensity effect. The variation between observers within the group is greatest in this chromaticity region; the individual's criterion for the classification is less stable. Narrow limits chosen for low signal intensities would require an appreciable shift toward the white at high intensities—for the same signal efficiency. Thus, no real advantage may be expected from further reduction in the chromaticity tolerances for orange and yellow. The range of the orange-yellow in set *P* may be made sufficiently broad to meet all practical requirements and yet maintain a satisfactory signal efficiency for the group of observers over the required intensity (or distance) range. It may be noted also, as shown in figure 9, that the signal efficiency of the orange and yellow does not improve for the higher signal intensities, so that an identification error made under actual service conditions would not be corrected necessarily by a closer approach to the signal light.

On the whole, these considerations all lead to the elimination of orange and the final choice of the set P colors as yielding the six-color system of highest efficiency under the prescribed service conditions. The source intensity for the purple signal must be sufficient, however, to gain the required distance range. The limits selected for the orange-yellow are based on the assumption that a low source intensity will be used so that the signal intensity is roughly comparable with the other signals in this respect, in accordance with the field tests of series 1. They should be shifted slightly to the right if the signal intensities of series 2 prevail in practice.

The limits selected for each signal on the special chromaticity scale are listed in table 8. The minimum source intensity for each signal light, for efficient color identification over the 950-foot range, is estimated from the data in figure 9 and also recorded in table 8. In the last column of this table these source intensities are reduced to equivalent signal intensities for a 1,500-foot range, using the average transmission values from figure 4 and the inverse-square law of photometry.

TABLE 8.—*Chromaticity tolerances and minimum signal intensities recommended for signal colors*

Signal color	Designation of limits	Trilinear coordinates						Minimum intensity	
		UCS system (Judd)			ICI system (standard)			Source for 950-ft range (candles)	Signal for 1,500-ft range (candles)
		r	g	b	x	y	z		
Red	Purple	0.993	0.007	0.000	0.733	0.267	0.000	3.	0.4
	Orange	0.944	.056	.000	.716	.284	.000		
Orange-yellow	Red	.766	.234	.000	.641	.359	.000	1.	1.2
	White	.680	.320	.000	.593	.407	.000		
White	Yellow	.497	.450	.053	.388	.383	.229	1.	1.0
	Blue	.455	.467	.078	.333	.347	.320		
Green	Yellow	.380	.605	.015	.274	.626	.100	3.	.6
	Blue	.343	.608	.049	.212	.516	.272		
Blue	Green	.233	.386	.381	.146	.055	.799	15.	.3
	Purple	.229	.345	.426	.150	.032	.818		
Purple	Blue	.270	.344	.386	.169	.049	.782	21.	.2
	Red	.276	.317	.407	.173	.038	.789		

It is evident that the experimental results of the present investigation do not define complete boundaries of regions on the color diagram of figure 2, within which a two-dimensional chromaticity variation is permissible for each signal color. In particular, considerable latitude in this respect is permissible in the establishment of such boundaries for the green. Only the intersections of such regions with the special linear chromaticity scale are roughly indicated in the present paper. Thus, only one yellow and one blue limit is suggested for the green. The lowest practical transmission for the filter used will determine the high saturation limits for this region, which is consistent with the maintenance of suitable signal intensities. All other signal colors of the system may be limited, by practical considerations in the choice of filters, to narrow strips centered along the linear chromaticity scale.

It is beyond the scope of the present paper to set up complete definitions for such chromaticity regions. The exact definitions, when incorporated in master specifications, will involve the choice of some particular coordinate system and simple analytical descriptions of the boundaries. These boundaries also may be adjusted to some degree to accommodate the colorimetric properties of such colored glassware most readily obtainable from manufacturers. Work is in progress on the formulation of such master specifications and simplified working specifications in terms of specific physical properties of the source and glassware.[14]

WASHINGTON, August 21, 1936.

[14] Such master specifications and simplified working specifications for the signal colors and glasses used on American railroads have already been formulated and are incorporated in AAR (Association of American Railroads) Signal Section specification 69-35, officially approved and issued by the AAR in Dec. 1935. The National Bureau of Standards cooperated in this investigation with the AAR Signal Section and with Corning Glass Works. The Bureau's work leading up to this specification is described in a series of reports by K. S. Gibson and Geraldine K. Walker, published in Signal Section proceedings, Am. Railway Association, 30, no. 2, 441 (1933). Requests for copies of specification 69-35 and the Proceedings should be addressed to R. H. C. Balliet, Secretary, AAR Signal Section, 30 Vesey Street, New York, N. Y.

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